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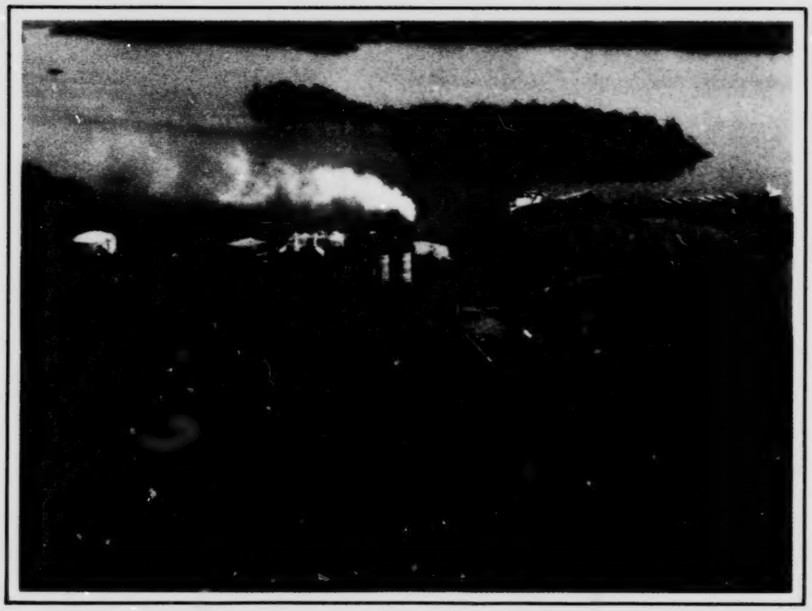
Canada Centre for Mineral and Energy Technology
Centre canadien de la technologie des minéraux et de l'énergie

Supplementary Cementing Materials
FOR CONCRETE



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V.M. Malhotra

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FOREWORD

The Canada Centre for Mineral and Energy Technology (CANMET) of the Department of Energy, Mines and Resources has played a prominent role in Canada for more than 30 years in the research and development associated with aggregates, cements and concretes. In recent years, the department has become involved increasingly in research in supplementary cementing materials. The use of pozzolans and slags as replacement for cement in concrete not only contributes to the energy conservation, because cement is one of the most energy intensive materials, but also helps towards the solving, to a degree, of the disposal problem of the by-product materials. CANMET maintains very close liaison with the cement and concrete industry in order to transfer technology effectively and promptly. Also CANMET, in association with the American Concrete Institute and Canadian Society for Civil Engineering, has been active in sponsoring national and international seminars, workshops and conferences in Canada and Europe to bring together representatives from industry, universities, and government agencies to present the latest information on supplementary cementing materials, to explore new areas of needed research, and to encourage the wide use of these materials in civil engineering construction.

It is hoped that the publication of this volume will contribute to a better understanding of new technology and will encourage its use by the cement and concrete industry.

W.G. Jeffery
Director General
CANMET
March 30, 1987

AVANT-PROPOS

Le Centre canadien de la technologie des minéraux et de l'énergie (CANMET) du ministère de l'Energie, Mines et Ressources, a joué depuis plus de 30 ans au Canada un rôle marquant dans la recherche et le développement reliés aux agrégats, aux ciments et aux bétons. Ces dernières années, le ministère s'est impliqué davantage dans la recherche de matériaux complémentaires du ciment. L'utilisation des pouzzolanes et des laitiers, à titre de matériaux de substitution du ciment dans le béton, non seulement contribue à la conservation de l'énergie, puisque le ciment est l'un des matériaux nécessitant beaucoup d'énergie pour sa production, mais aussi parce qu'il aide, jusqu'à un certain point, à résoudre le problème de l'élimination de ces sous-produits. Le CANMET maintient une liaison très étroite avec les industries du ciment, du béton et des mines dans le but d'effectuer efficacement et rapidement des transferts de technologie. De plus, le CANMET, en association avec l'Institut américain du béton et la Société canadienne de génie civil, a été très actif dans le parrainage de séminaires nationaux et internationaux, d'ateliers et de conférences au Canada et en Europe, de façon à rassembler des représentants des industries, des universités et des agences gouvernementales, dans le but de présenter les informations les plus récentes sur les matériaux complémentaires en cimentation, explorer de nouvelles avenues de recherche et encourager une large utilisation de ces matériaux dans les constructions d'ingénierie civile.

Nous espérons que la publication de ce volume contribuera à une meilleure compréhension de ces nouvelles technologies et encouragera leurs utilisations par les industries du ciment et du béton.

W.G. Jeffery
Directeur général
CANMET
30 Mars 1987

PREFACE

This volume brings together seven comprehensive state-of-the-art papers on supplementary cementing materials for use in concrete. Internationally recognized experts from Canada, Norway and the United States were invited to contribute papers on the subject.

The book opens with a paper on natural pozzolans, a material which has been in use for over 2000 years. This is followed by a paper on fly ash, a pozzolanic by-product of the combustion of pulverized coal in thermal power stations, which is finding increasing acceptance for use in concrete the world over. The third paper deals with a worldwide review of a relatively new material known as condensed silica fume. This material is highly pozzolanic and is a by-product resulting from the reduction of high purity quartz with coal in electric arc furnaces in the production of silicon and silicon alloys. The next four papers deal with ferrous and non-ferrous slags. The ground granulated blast-furnace slags, though in use in Europe for over seventy-five years, are relatively new in North America and offer great potential for use in concrete. The non-ferrous slags, particularly copper, zinc, and lead slags, are of interest to Canada because of the large volumes available in the country.

The editor wishes to thank the authors for the comprehensive nature of their papers, and for their co-operation in meeting the printer deadlines. Particular thanks are extended to Ms. M. Close of the Technical Information Division, CANMET, for the processing of this publication, and to Ms. V. Sivasundaram of Mineral Sciences Laboratories, CANMET, for her assistance in reviewing several of the contributions.

V.M. Malhotra
Editor
March 1987

PRÉFACE

Le présent volume rassemble sept articles détaillés sur l'état d'avancement des connaissances concernant les matériaux complémentaires du ciment utilisés dans le béton. Des experts de réputation internationale, provenant du Canada, de la Norvège et des États-Unis, ont été invités à rédiger des articles sur le sujet.

Le volume débute avec un article portant sur les pouzzolanes naturels, un matériau qui est utilisé depuis plus de deux milles ans. Il est suivi par un article sur les cendres volantes, un sous-produit pouzzolanique qui est tiré de la combustion dans les centrales thermiques du charbon pulvérisé et dont l'utilisation dans le béton est de plus en plus acceptée à travers le monde. Le troisième article traite d'une revue mondiale d'un matériau relativement nouveau connu sous le nom de vapeur de silice condensée. Ce matériau est hautement pouzzolanique et est un sous-produit provenant de la réduction de quartz très pur avec du charbon dans des fournaises à arc électrique, lors de la production de silicium et d'alliages au silicium. Les quatre articles suivant discutent des laitiers ferreux et non-ferreux. Les laitiers de haut-fourneau en terre granulée, malgré le fait qu'ils sont utilisés en Europe depuis plus de 75 ans, sont relativement nouveaux en Amérique du nord et présentent un grand potentiel pour utilisation dans les bétons. Les laitiers non-ferreux, en particulier ceux de cuivre, de zinc et de plomb, sont très intéressants pour le Canada à cause des grandes quantités disponibles dans le pays.

L'éditeur souhaite remercier les auteurs pour l'aspect détaillé de leurs articles et pour le respect des échéances d'imprimerie qu'ils ont su respecter. Ajoutons un merci particulier à Mme M. Close de la Division de l'information technologique, CANMET, et à Mme V. Sivasundaram des Laboratoires des sciences minérales, CANMET, pour son aide dans la révision de plusieurs articles.

V.M. Malhotra
Editeur
Mars 1987

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CHAPTER 1

NATURAL POZZOLANS

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1. INTRODUCTION

The recent volcanic eruption in Colombia in which more than 20 000 people died shows that volcanic eruptions can be highly destructive. In May 1980, the eruption of Mount St. Helens in Washington State laid waste 500 square kilometres of forests, streams, and lakes. About 400 million metric tons of volcanic ash and rock were hurled into the environment and the ash clouds covered the skies in the northwest United States for several days.

In 79 A.D., a similar volcanic eruption at Mount Vesuvius in Italy engulfed Herculaneum, Pompeii, and many other towns along the Bay of Naples with ash, pumice, and mud causing death and destruction on a large scale. In 1500 B.C., a powerful volcanic eruption in the Greek island of Santorini produced so much lava and ash that waves as high as 80 to 100 m were generated in the Agean sea resulting in the total destruction of the well-developed Minoan civilization.

However, not all the consequences from volcanic eruptions are bad. Under hydrothermal conditions, volcanic ash is transformed into zeolitic tuff and, eventually, into clay minerals that constitute agricultural soils. Also, long ago it was discovered that volcanic ash or pulverized tuff, when mixed with lime, produced calcium silicate hydrates that are not only cementitious but also hydraulic (i.e., water resistant). Ancient structures in Greece and Italy provide sufficient evidence of the durability of pozzolan–lime cements.

For the construction of aqueducts, bridges, buildings, and waterfront walls, the Romans made wide use of a zeolitic tuff found in the foothills of Mount Vesuvius at Pozzuoli. Thus, this material was popularly known as pozzolana. When similar volcanic materials that reacted with lime were discovered in Germany, France, Spain, and other parts of the world, the term *pozzolana* or *pozzolan* was employed to designate any material, regardless of its geological origin, which would react with lime to produce a cementitious product. Until the advent of the calcium silicate cements (portland cement) in the 19th century, pozzolan–lime mixtures were the primary cementing materials for the construction of masonry and hydraulic structures throughout the world.

Unlike volcanic glass and zeolitic tuff, clay minerals do not readily react with lime unless their crystalline structure is destroyed by heat. Thus geographical constraint to the production of pozzolan–lime cements was removed when it became obvious that pozzolans can be made by heat treatment of non-pozzolanic clays and shales. Diatomaceous earths, consisting of opaline or amorphous hydrated silica, were also found to exhibit excellent pozzolanic characteristic. However, they are generally contaminated with clay and, therefore, have to be calcined to enhance the lime-reactivity.

According to ASTM C 618, a pozzolan is defined as a siliceous or siliceous and aluminous material which, in itself, possesses little or no cementitious value but which will, in finely divided form and in the presence of moisture, react chemically with calcium hydroxide *at ordinary temperature* to form compounds possessing cementitious properties. This definition rules out ordinary quartzite sand being categorized as a pozzolan, because mixtures of pulverized sand and lime require hydrothermal treatment to form cementitious products. However, the definition of a pozzolan includes several industrial by-products, such as fly ash, rice husk ash, and condensed silica fume, which can react with lime at ordinary temperature.

Since the advent of portland cement in the 19th century, pozzolan–lime mixtures are seldom used for making structural concrete because portland cement sets and hardens at a considerably faster rate than pozzolan–lime mixtures. Portland cement consists mainly of tricalcium and dicalcium silicates which, on hydration, produce calcium silicate hydrates and calcium hydroxide. Because calcium hydroxide is not a cementitious material, it can only be converted into one if a pozzolan is added to the concrete mixture. This addition can be achieved either by blending the pozzolan with the portland cement or by using the pozzolan as a direct admixture to concrete.

Regardless of how a pozzolan is used, the pozzolanic reaction and the benefits associated with it remain the same. The main technical advantages from the use of pozzolans in portland cement concrete include improvement in workability, reduced heat of hydration and risk of thermal cracking, increased water tightness, better durability to sulphate and acidic environments, and enhanced resistance to cracking by alkali–aggregate reaction.

2. HISTORY OF THE USE OF NATURAL POZZOLANS IN THE WORLD

Before the invention of portland cement in 1824, pozzolan–lime mortars and concretes were in use throughout the world. After portland cement became available, the use of pozzolan–lime mixtures for cementitious purposes declined gradually because of their relatively slow setting and hardening characteristics. However, for economic reasons and to achieve certain technical benefits, mixtures of portland cement and pozzolans are still commonly used in concrete construction. The history and the use of natural pozzolans in some countries of the world are described in the following paragraphs.

According to Lea (1) there is evidence that the Minoan structures of Crete Island, built about 1500–2000 B.C., contained crushed potsherds (i.e., calcined clay) in a lime mortar. The use of natural pozzolan–lime concrete has been discovered in a lining for a water tank dating from 600–700 B.C. in the ancient Greek city of Camiros, Rhodes Island. According to Effstathiadis (2), volcanic ash from Santorini, called Santorin earth, was used for making the concrete for the Suez canal lining, which is still hard and in a durable condition. As a pozzolanic material it still enjoys high reputation on the Mediterranean. For reasons of economy and energy conservation, all portland cement produced in Greece routinely contains 10% Santorin earth. It is estimated that for this purpose the yearly consumption rate of natural pozzolans is of the order of 800 000 metric tons.

It is well known now that the Romans widely practised the art and science of building construction developed by the Greeks. Volcanic materials similar in properties to Santorin earth were discovered in Pozzuoli at the Bay of Naples and in Segni, which is in the Latium District near Rome. According to Lea (1), the Romans may also have used pozzolans from crushed tiles before they discovered the deposits in Pozzuoli and Segni. They seem to have carried their knowledge of preparing moisture-resistant mortar from pozzolan–lime mixtures to all parts of their empire including Germany, France, and Britain. The Rheinisch trass in Germany, a volcanic tuff, was probably discovered during the Roman period. In addition to concrete lining for aqueducts, as described by Malinowski (3), pozzolan-lime concrete was widely used by the Romans for the construction of cisterns, waterfront walls, and brickwork in buildings.

One of the most famous Roman buildings is the Pantheon, the 7-m thick walls of which are made of pozzolan–lime cement mortar thinly faced with brick, while the large dome (43-m span) is cast solid in concrete containing pumicite pozzolan. Many of the Roman structures remain in excellent condition even today, and thus serve as a testimony to the long-term durability of well-made pozzolan–lime cement products. It may be noted that during the 9th–12th century period, the art of making lime of a proper quality was lost in Europe (1), however after the 15th century it was gradually reestablished. The pozzolan–lime concrete, such as the one used in the Palace of Versailles, is of excellent quality.

According to Collepardi (4), a considerable amount of natural pozzolan is still used in Italy. In 1984, the total cement production of Italy was 36 million metric tons and about 40% of the cement was of the portland–pozzolan type containing 25% pozzolan. Therefore, 3.5 million metric tons of pozzolans are being used annually for making blended portland cement. Further, according to Collepardi, about 85% (3 million metric tons) of the pozzolan used comes from natural sources, the rest being fly ash.

The Rheinisch trass mentioned above, is found in the neighborhood of Koblenz on the Rhine river and in Bavaria. Trass deposits are also found in Romania and the Soviet Union. According to Lea (1), the Rheinisch trass has been known for about 2000 years because mortars containing the trass have been found in old Roman buildings along the Rhine. Since about the end of the 17th century, Rheinisch trass has been widely used, first in pozzolan–lime cements and later as a portland cement additive.

In the Federal Republic of Germany, trass has been standardized in DIN 51043, which differentiates between the *Rheinischer Trass* and the *Bayrischer Trass*. The latter, according to Locher (5) was originally a sedimentary rock but was transformed to suevite by the impact of a meteriorite. Another zeolitic rock called phonolite, which is found in southwest Germany near Freiburg, is used as a pozzolan. However, it becomes sufficiently reactive to lime only after calcination between 300 and 600°C (6). The amount of pozzolan cements produced in Germany today is not large. Locher estimates that in 1984 about 40 000 metric tons of trass and 10 000 metric tons of phonolite were used for making blended portland cements.

In the United States, according to Price (7), the first large use of the portland–pozzolan cement, composed of equal parts by volume of a portland cement and a deeply altered rhyolite tuff, was made in the construction of Los Angeles aqueduct, where about 1 × 10^5 metric tons of the cement were employed during the years 1910 to 1912. Meissner (8) reported that the Santa Cruz Cement Company at Davenport, California, produced a portland–pozzolan cement containing calcined Monterey shale as a pozzolanic ingredient. In the 1930's, the cement was used by the California Division of Highways in several structures including the Golden Gate Bridge and the San Francisco–Oakland Bay Bridge. The main reasons for the use of this cement was its proven resistance to sulphate water together with the favorable heat generation characteristics in massive blocks of concrete. In 1935, a portland–pozzolan cement was used in the construction of Bonneville Dam which is located on the Columbia River between Oregon and Washington states.

The first application of a natural pozzolan as a mineral admixture was in the 1920's when a raw rhyolite pumicite was used in one of the abutments of Big Dalton Dam by the Los Angeles Flood Control District, as a 20% by weight replacement of the portland cement. In the 1930's, this organization made similar use of the material in several other structures.

In 1933, the U.S. Bureau of Reclamation undertook an intensive study on utilization of natural pozzolans for the purpose of controlling the heat of hydration of concrete for large dams. According to Mielenz (9), as a result of the Bureau's investigation, rhyolitic pumicite was used as an admixture in concrete for the construction of Friant Dam on the San Joaquin River, and Altus Dam in Oklahoma. Later in 1947, a calcined, siliceous pozzolan was used as a mineral admixture in Davis Dam (Nevada–Arizona), primarily to control alkali–aggregate reaction. Other applications of natural pozzolans in the western United States included Glenn Anne, Cachuma, Trenton, Monticello, Glenn Canyon, Flamingo Gorge, Falcon, Priest Rapids, Wanapum, and John Day dams. Mielenz further reports that materials suitable for use as pozzolans, either by calcination and grinding or by grinding alone, are widespread in the United States, but that tested sources are mainly west of the Mississippi River. In many cases, pozzolans of natural origin were produced for a specific project but the operation was abandoned after completion of the work. Portland–pozzolan cements composed of natural pozzolans are no longer being produced in the United States.

Among the countries where blended portland cements containing natural pozzolan continue to play an important role in the construction industry are China and Mexico. According to Wu (10), zeolitic tuff and calcined coal shale are the main sources of natural pozzolan in China. It is estimated that in l984 China produced 90 million metric tons of cement containing over 5 million metric tons of zeolitic rock and 6 million metric tons of calcined coal-shale. Wu believes that, in 1990's because of the increasing demand for cement in China, the amount of natural pozzolan used for cement production is bound to increase substantially.

Similarly, in Mexico about one-third of the total cement used every year is a blended portland cement containing natural pozzolan. Ten years ago the annual cement consumption of Mexico was 10.6 million metric tons and about 13% of the cement was of the blended variety containing a natural pozzolan. In 1984, Mexico consumed 18.3 million metric tons of cement including 6.3 million metric tons (34.2%) of blended portland cement containing natural pozzolans. According to Poo (11) several forms of natural pozzolans are found in different regions of Mexico, such as pumicite in Jalisco, diatomite in Baja California, and zeolitic tuff in Guanajuato.

3. CLASSIFICATION AND COMPOSITION

It is not always easy to classify a natural pozzolan because natural materials seldom contain only one lime-reactive constituent, and their composition and properties vary widely. However, based on the principal lime-reactive constituent present, the natural pozzolans can be classified into four categories, i.e., unaltered volcanic glass, volcanic tuff, calcined clay or shale, and raw or calcined opaline silica. Typical oxide analyses and mineralogical descriptions of some of the well-known pozzolans in the world are given in Tables 3.1 and 3.2, respectively.

Table 3.1 — Typical chemical analyses of some natural pozzolans

	Per cent							
Pozzolan	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	Alkalis	Ignition loss	Reference
Santorin earth	65.1	14.5	5.5	3.0	1.1	6.5	3.5	12
Rheinish trass	53.0	16.0	6.0	7.0	3.0	6.0	—	5
Phonolite	55.7	20.2	2.8	4.2	1.1	10.8	3.6	6
Roman tuff	44.7	18.9	10.1	10.3	4.4	6.7	4.4	13
Neapolitan glass	54.5	18.3	4.6	7.4	1.0	11.0	3.1	13
Opaline shale	65.4	10.1	4.2	4.6	2.7	1.4	6.3	15
Diatomite	86.0	2.3	1.8	—	0.6	0.4	5.2	15
Rhyolite pumicite	65.7	15.9	2.5	3.4	1.3	6.9	3.4	15
Jalisco pumice	68.7	14.8	2.3	—	0.5	9.3	5.6	11

Table 3.2 — Mineralogical analysis of some natural pozzolans

Pozzolan	Estimated non-crystalline matter, %	Major crystalline minerals	Reference
Santorin earth	65–75	quartz, anorthite, labradorite	12, 24
Rheinisch trass	50–60	quartz, feldspar, analcine	16
Phonolite	*	orthoclase, albite, pyroxene, calcite	6
Roman tuff	*	herschellite, chabazite, phillipsite	1
Neapolitan glass	50–70	quartz, feldspar	20
Jalisco pumice	90	sanidine	11

*not reported.

Volcanic Glass

Natural pozzolans that are composed of volcanic glass derive their lime-reactivity mainly from unaltered aluminosilicate glass. Examples are pozzolans from Santorini (Greece), Bacoli (Italy), Shirasu (Japan), Jalisco (Mexico), and rhyolitic pumicites found in several western states of the United States.

Mineralogical analyses show that small amounts of non-reactive crystalline minerals are invariably present in the natural pozzolans. Figure 3.1 shows an X-ray diffractogram of a typical sample of Santorin earth (12). Typically, the material consists of about 80% volcanic glass (pumice and obsidian) and 20% quartz and feldspar (anorthite and labradorite). Similarly, according to Massazza and Costa (13), the vitreous or glassy matrix of the Bacoli pozzolan contains inclusion of several crystalline minerals, such as leucite, feldspar, and augite. Takemoto and Uchikawa (14) reported the mineralogical analysis of a specimen of the Shirasu pozzolan from Japan, which contained 95% glass with quartz and feldspar as the principal crystalline impurities.

According to Poo (11), the Jalisco pozzolan of Mexico, typically consists of about 90% pumice glass and 10% sanidine feldspar. Of the 70 materials from the western United States investigated for pozzolanic activity by Mielenz et al. (15), 12 owed their pozzolanic activity almost exclusively to rhyolitic glass. In addition, 10 materials owed a significant portion of their activity to volcanic glass. According to the authors, as a pozzolan *basaltic glass appears to be inferior to the acidic glasses*, such as rhyolite and andesite.

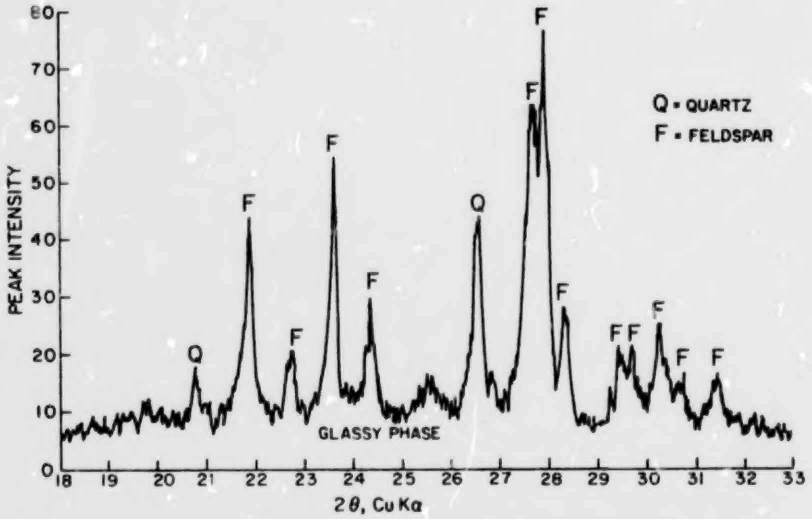


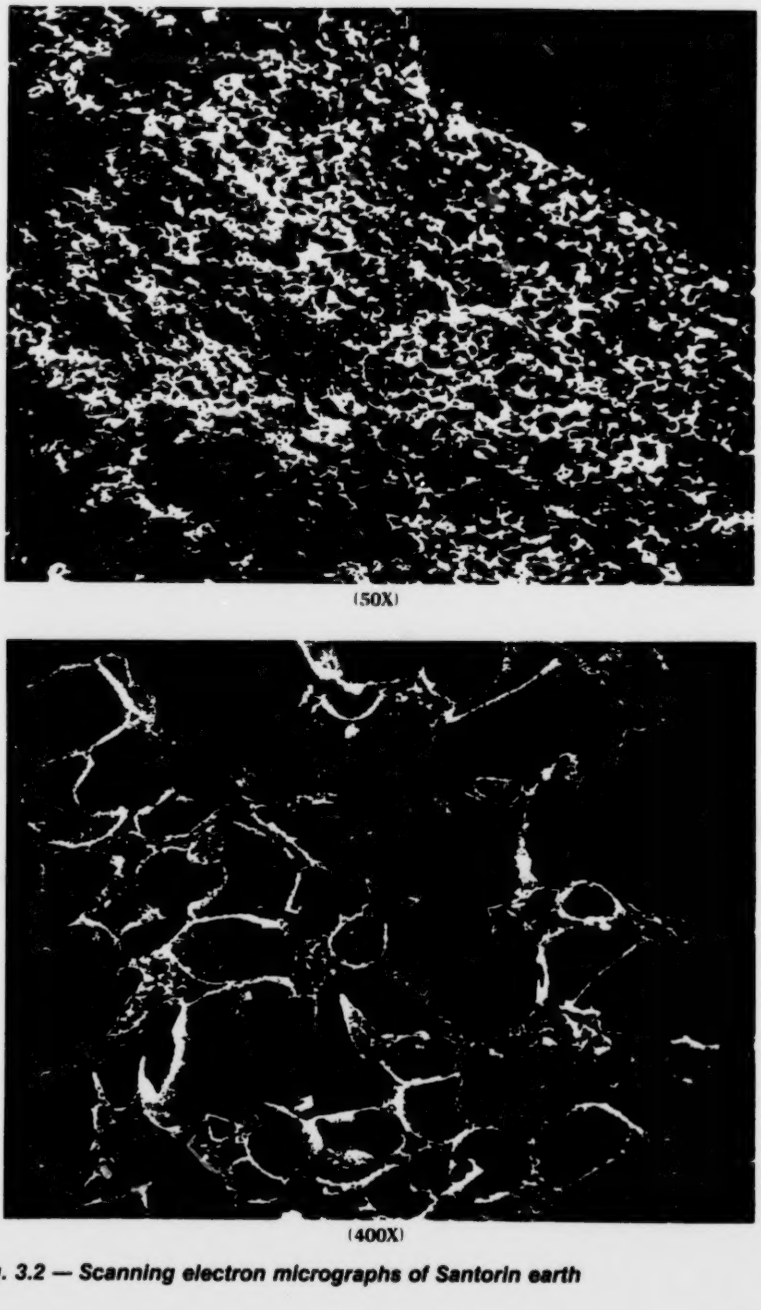
Fig. 3.1 — X-ray diffraction analysis of Santorin earth

The typically microporous texture of the volcanic glass is evident from the scanning electron micrograph of a specimen of Santorin earth (Fig. 3.2). In addition to the disordered or glassy structure, the high surface area is responsible for the chemical reactivity of the material. Surface area analyses of several samples of Santorin earth by the BET nitrogen adsorption technique gave values in the range 3800 to 15 500 m^2/kg (12).

Volcanic Tuff

The alteration of volcanic glass under hydrothermic conditions leads to the formation of zeolitic minerals with variable chemical composition of the type, $(R_2Ca)O{\cdot}Al_2O_3.4SiO_2{\cdot}xH_2O$, where R stands for Na or K. Volcanic tuffs are the product of hydrothermal action on volcanic ash, and are characterized by a hard and compact texture. Unlike volcanic glass, the reactivity of zeolitic minerals with lime is attributed to a base-exchange process between calcium (lime) and the alkalis from the volcanic tuff. In general, natural pozzolans that derive their lime-reactivity from base exchange reaction are categorized as volcanic tuffs.

According to Lea (1), the zeolitic compounds commonly found in altered volcanic glass are analcite, chabazite, herschellite, and phillipsite. Analcite corresponds to the chemical composition, $Na_2{\cdot}Al_2O_3{\cdot}4SiO_2{\cdot}H_2O$, chabazite to $(R_2Ca)O{\cdot}Al_2O_3{\cdot}4SiO_2{\cdot}6H_2O$, herschellite to a corresponding compound richer



(50X)

(400X)

Fig. 3.2 — Scanning electron micrographs of Santorin earth

in alkalis, and phillipsite to a potassium-rich compound. The Roman pozzolans from the Calleferro region contain herschellite, chabazite, and phillipsite, whereas the Neapolitan tuffs contain herschellite, analcite, and glauconite ($K_2O \cdot Fe_2O_3 \cdot 4SiO_2 \cdot xH_2O$).

The mineralogical analysis of the Rheinisch trass as reported by Schwiete et al. (16), shows that it contains 10–15% quartz, 15–20% feldspar, small amounts of kaolinite and montmorillonite, and about 50% of glassy matrix that has undergone alteration to zeolitic minerals. From Freiburg in southwestern Germany comes another pozzolan, called phonolite, which derives its hydraulic reactivity from zeolites belonging to natrolite group. According to Kassautzki (6), a marked increase in the hydraulic reactivity of phonolite is obtained after calcination at 300 to 600°C.

In the United States, many of the 70 specimens investigated for pozzolanic activity by Mielenz et al. (15) contained altered rhyolitic tuff. Two Californian pozzolans, from Monolith and Coachella, owed their pozzolanic activity essentially to the altered rhyolitic tuff containing no volcanic glass but including clinoptilolite (silica-rich heulandite). The Mexican pozzolan from the Guanajuato region is a zeolitic tuff containing clinoptilolite, quartz, and feldspar (11).

Calcined Clay or Shales

Volcanic glass and tuff do not require calcination to enhance the lime-reactivity, however, natural materials consisting essentially of clay minerals require heat treatment. When heated to temperatures in the order of 600 to 1000°C (usually in an oil-, gas-, or coal-fired rotary kiln) the clay minerals decompose to form an amorphous or a disordered aluminosilicate structure that reacts readily with lime at ordinary temperature. Surkhi in India and hombra in Egypt, produced by pulverizing baked-clay tile or brick, also belong to this category. However, any baked-clay product may not produce a good pozzolan. The heat treatment of a clay or shale that contains large amounts of highly crystalline minerals, such as quartz and feldspar, would not produce a material possessing adequate reactivity with lime.

According to Mielenz (9) natural materials that include substantial proportions of kaolinite-type or montmorillonite-type clay minerals, or combinations thereof, require calcination at temperatures in the range of 540 to 980°C to induce optimum pozzolanic activity. However, montmorillonite clay in which a large amount of exchangeable sodium cation is present should be avoided, especially if the aggregates proposed for use in the concrete are susceptible to a deleterious degree of alkali–aggregate reaction. Illitic clays and shales containing substantial proportions of vermiculite, chlorite, and mica are generally not suitable sources of pozzolans when the calcination temperature is below 1100°C.

Opaline Silica

Opaline materials including diatomaceous earths and silica gel belong to this category. Diatomaceous earths are of organogen origin. They contain hydrous, non-crystalline silica composed of skeletal shells from the cell walls of many varieties of microscopic aquatic algae. Opal is generally formed as a hydrated silica gel in sediments when the soluble oxides have been leached away from the minerals.

Large deposits of diatomaceous earth are found in Algiers, Canada, Denmark, Germany, India, Mexico, and the United States. Nine of the 70 materials tested for pozzolanic activity by Mielenz et al. (15) were diatomites from the states of California and Washington; two materials owed their pozzolanic activity wholly to opal (gelatinous or non-crystalline silica) mixed with beta cristobalite, and many other materials owed a significant proportion of their activity to opaline chert, sandstone, or shale.

Opaline materials are very reactive to lime but their large surface area results in unusually high water requirement in concrete mixtures, which is harmful to strength and durability. Furthermore, they generally contain large amounts of clay minerals. To enhance the use of such materials as pozzolans, it is often necessary to calcine them.

Gaize is a soft and highly siliceous sedimentary rock containing some clay, which is found in the Ardennes and Meuse valleys in France. The material contains silica in gelatinous condition and can be used in the raw state as a pozzolan, but it is more suitable when calcined at a temperature of about 900°C. Lea (1) reported that a portland-pozzolan cement containing burnt gaize was used at Boulogne, Havre, St. Malo, Dieppe, and other French ports for making concrete structures exposed to sea water.

Moler, a Danish pozzolan, is a diatomite containing a large amount of clay. According to Lea, a moler cement containing 75% portland cement and 25% moler was manufactured in Denmark and used for concrete structures exposed to sea water. Initially, raw moler was used, but later burnt moler was found to be superior and was used, instead of the raw product.

Airox, a proprietary product produced in Santa Maria, California, by calcination of an oil-impregnated diatomaceous shale, is subsequently ground to a surface area in the order of 12 000 m^2/kg (by BET nitrogen adsorption). A sample of this material showed excellent pozzolanic activity as required by the ASTM C 618 Specification, i.e., 9.5 MPa (1370 psi) compressive strength in 7 days in the pozzolan–lime mortar, and 4540 psi compressive strength in 28 days in the portland cement–pozzolan mortar (17).

4. THERMAL ACTIVATION OF RAW POZZOLAN

Many natural pozzolans can be used in the as-mined or raw state after removal of coarse (> 75-μm) particles. Moist materials may have to be dried and pulverized before use. Zeolitic rock has to be crushed and ground to a particle size mostly below 75 μm. Calcination of zeolitic tuff or opaline shale may not enhance the pozzolanic activity unless a significant proportion of clay minerals are present. However, to develop an acceptable level of pozzolanic activity, clays and shales, or pozzolanic materials containing substantial amount of clay or shale, must be thermally activated (i.e., calcined).

Mielenz et al. (15) made a comprehensive study of the effect of thermal activation on different types of pozzolans. Of the 70 materials investigated, 12 owed their activity primarily to volcanic glass with 70–73% SiO_2 content. The content of rhyolitic glass in these 12 pozzolans ranged from 40 to 100%. In addition, ten materials owed a significant portion of their activity to volcanic glass. Through hydrothermal alteration and weathering, the original glass in most of the volcanic pozzolans had been changed generally to montmorillonite-type clays, or less commonly to kaolinite-type clay or zeolite. Consequently, the response of volcanic glasses to heat treatment depended on the amount of clay minerals present. It was concluded that the physical properties and pozzolanic activity of volcanic glass-type pozzolans were only slightly affected by calcination to temperatures as high as 1000°C.

Eleven of the 70 materials investigated by Mielenz et al. (15) belonged to the category of hydrous amorphous silica (i.e., diatomites and opaline cherts and shales). Calcination to about 450°C caused no change in properties and activity but calcination to 1100°C produced significant changes in behavior. For the materials calcined to 750–1000°C, the setting times of the portland cement–calcined pozzolan mixtures were significantly reduced and the compressive strengths were significantly improved, but this improvement in the pozzolanic behavior was lost at the higher calcination temperatures. It seems that the dehydrated amorphous silica structure was more reactive than the hydrous form. Also, partial sintering reduced the surface area of the natural material; thus the lower water requirement of the partially sintered material was responsible for reduction in the setting time and for increase in strength of the portland–pozzolan mixtures. The pozzolanic behavior of opaline materials appeared to be quite sensitive to the temperature of calcination, because calcination at 1100°C increased the setting time and decreased the strength, probably as a result of over-sintering associated with a substantial loss of activity.

Thirteen of the materials investigated by Mielenz et al. (15) contained montmorillonite as the essential ingredient, 3 contained essentially kaolinite, and 15 contained a mixture of clay minerals including illite and vermiculite. The authors concluded that calcination of clayey materials was essential to develop satisfactory pozzolanic activity, however, the response to heat treatment varied with the type of clay minerals present. The hydrous aluminum silicates of the kaolinite group lost the water of hydration between 320 and 500°C and, thereafter, showed significant increase in pozzolanic activity, although above 900°C a reduction in the surface area caused a drop in the activity. At very high temperatures, non-reactive crystalline minerals such as mullite were formed.

The minerals of the montmorillonite group lost most of the water of crystallization between 150 and 510°C; the dehydration was essentially complete by 650°C but the crystal structure was not destroyed until about 870°C. Correspondingly, optimum strength and setting-time properties in portland cement–calcined montmorillonite mixtures were obtained when calcination temperatures were in the range of 650 to 870°C. Illite and vermiculite-type clays were not found to be very promising from the standpoint of strength development. Also, a zeolitic tuff containing 80% clinoptilolite showed some improvement in pozzolanic activity after calcination.

Jun-yuan et al. (18) described the results of an investigation on the effect of heat treatment on a zeolitic tuff obtained from near the Nevada Test Site. The material consisted mainly of clinoptilolite and sanidine, with quartz and plagioclase feldspar present as minor phases. The natural tuff was calcined in a muffle furnace to 400°, 600°, 800°, and 950°C for two hours. The compressive strengths of 29-day-old portland cement mortars both with and without natural or calcined pozzolan (35% cement replacement by volume in the test mortar), were determined. Although the effect of thermal treatment on the strength of tuff-bearing cements was not found to be remarkable compared to the natural or uncalcined tuff, a slight increase in the strength of mortars containing tuff calcined at 400 to 600°C was noticed. Also, it was found that the reactivity of tuff calcined at 800°C was decreased due to reduction in the surface area as a result of partial sintering.

5. THE POZZOLANIC REACTION

ASTM C 618 chemical requirements for natural pozzolan prescribe that for use with portland cement concrete the sum of SiO_2, Al_2O_3, and Fe_2O_3 must be at least 70%. It is assumed that in a mixture of portland cement with pozzolan and water, when SiO_2, Al_2O_3, and Fe_2O_3 in the pozzolan are present in an amorphous or poorly crystalline structure, these oxides will react chemically at ordinary temperature with calcium hydroxide (produced by the hydration of calcium silicates in portland cement) to form compounds possessing cementitious properties. Except for zeolites, which develop their cementitious property with lime by a base-exchange mechanism as already described, it is the acid–base reactions between lime and the acidic oxides of a pozzolan that are mostly responsible for technical improvements in concrete containing the pozzolan.

Natural pozzolans generally contain 60 to 85% SiO_2 (see Table 3.1), so the main pozzolanic reaction involves the formation of calcium silicate hydrate (CSH)*, similar to that produced by the hydration of the principal calcium silicate compound (i.e., C_3S) of portland cement:

(1) $CH + S + aq \rightarrow CSH$ (the pozzolanic reaction)

(2) $C_3S + aq \rightarrow CSH + CH$ (portland cement hydration).

The pozzolanic reaction is slow, so the rate of the strength development and the heat of hydration associated with this reaction are low. On the other hand, the hydration of C_3S in portland cement is fast, so the strength development rate and the heat of hydration associated with it are high. It should also be noted that the former is a lime-*consuming* reaction, whereas the latter is a lime-*producing* reaction.

Although the principal pozzolanic reaction is the chemical reaction involving lime and silica, it has been pointed out earlier that cementitious products are also formed as a result of the chemical reactions between lime and alumina or iron oxide. Typically, these products consist of calcium aluminate hydrates or calcium aluminoferrite hydrates. Because portland cement–pozzolan mixtures also contain sulphate (as the interground gypsum in portland cement), calcium sulphoaluminate and sulphoaluminate ferrite hydrates may form instead. Thus the essential difference between the pozzolanic reactions and the reactions involving the hydration of portland cement alone is not in the composition of the hydration products but the rate at which these are formed. It may be noted that the pozzolanic reactions can be accelerated by temperature, and by the presence of chemical admixtures, such as alkalis and sulphates.

6. CHEMICAL AND PHYSICAL MANIFESTATIONS OF THE POZZOLANIC REACTION

According to Turriziani (19), at ordinary temperature calcined kaolin and calcium hydroxide react to form gehlenite hydrate (C_2ASH_8) and a calcium silicate hydrate (CSH) of variable CaO to SiO_2 ratio which ranges from 0.8 to 1.5. However, Massazza and Costa (20) used several varieties of Italian pozzolans and concluded that the ratios of CaO to SiO_2 and H_2O to SiO_2 in the 90-day reaction product were 1.20 to 1.68 and 1.67 to 2.61, respectively, which are in the composition range of CSH formed by the hydration of C_3S (the principal compound in portland cement).

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*Cement chemistry notations are used: C = CaO, S = SiO_2, A = Al_2O_3, F = Fe_2O_3, $\bar{S}$ = SO_3, H = H_2O.

When a mixture of portland cement and a pozzolan is hydrated, with the progress of the pozzolanic reaction a gradual decrease of the free calcium hydroxide with time occurs (Fig. 6.1). For instance, the free calcium hydroxide content in the one-year-old hydrated cement pastes containing 10, 20, or 30% Santorin earth was found to be 13.0, 11.2, and 8.4%, respectively, as compared to 16.2% for the reference portland cement paste (12). This difference shows that in the 30% Santorin earth cement, up to 25% of the available calcium hydroxide had been consumed by the pozzolanic reactions. In summary, compared to a well-hydrated portland cement paste, the corresponding paste containing a pozzolan will contain less calcium hydroxide and more CSH. Additionally, it has been suggested (13) that the ratio of CaO to SiO_2 in the CSH present in a hydrated portland–pozzolan cement is somewhat lower than the CSH present in hydrated portland cements, and this may partly account for the superior chemical resistance of the former.

Recent work by many researchers has confirmed that, rather than the chemical manifestation, the physical manifestation of the pozzolanic reaction which involves *pore refinement* of the cement paste is probably more important for the enhancement of chemical durability and mechanical strength. Pore-size distribution plots were obtained with mercury intrusion porosimetry on 28-day, 90-day, and one-year-old pastes containing portland–Santorin earth cements (12). The data from the pore-size distribution analysis, arbitrarily divided into pore volumes <45Å, 45–500Å, 500–1000Å, and >1000Å, are illustrated in Figure 6.2. There is evidence that large pores (i.e., >1000Å or perhaps >500Å) are associated with lower strength and higher permeability. The data showing the effects of the age of hydration and amount of pozzolan present in the cement paste on a three-hour water penetration test are given in Table 6.1.

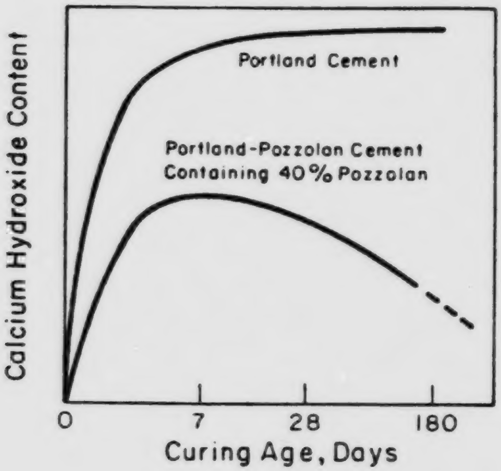


Fig. 6.1 — Changes in the calcium hydroxide content of a hydrating portland–pozzolan cement (1)

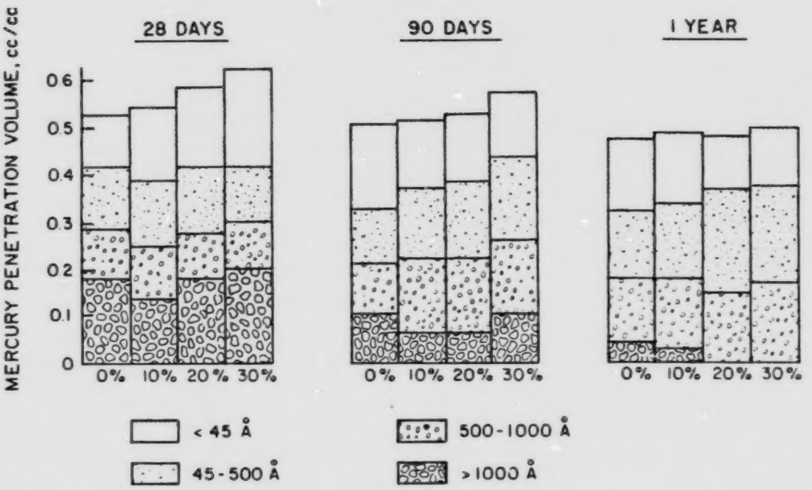


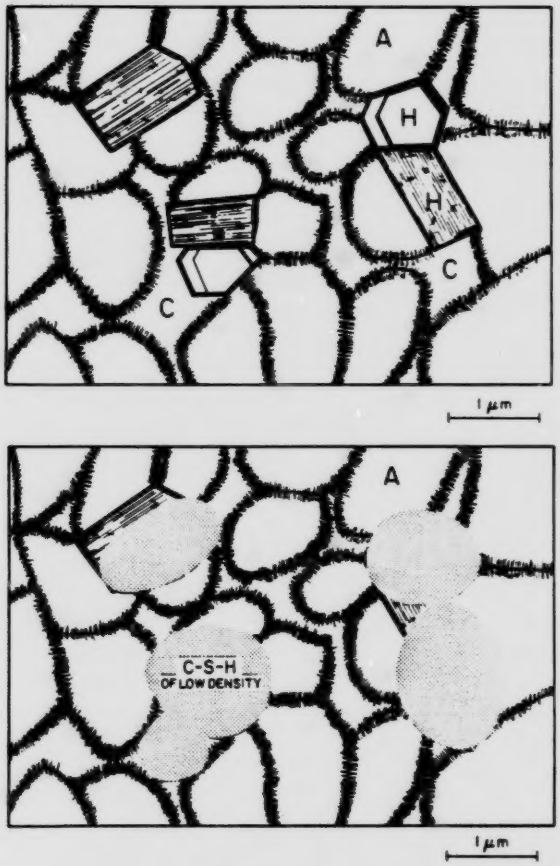
Fig. 6.2 — Pore size distribution of hydrated cement pastes containing various amounts of Santorin earth (12)

Table 6.1 — Relative depth of penetration of water into hydrated cement pastes*

	Depth of penetration, mm			
Hydration age	Portland cement	10% Santorin earth	20% Santorin earth	30% Santorin earth
28 days	26	24	25	25
90 days	25	23	23	22
1 year	25	23	18	15

*Reference 12.

It may be observed that significant reduction in water permeability was obtained for cements containing 20 or 30% pozzolan (at age one-year) when the process of pore refinement, i.e., the conversion of >1000Å pores to smaller pores, was essentially complete. A diagrammatic representation of reduction in large capillary pores as a result of the formation of the products of the principal pozzolanic reaction (CH + S → CSH) is shown in Figure 6.3.



A represents aggregation of poorly crystalline C-S-H particles which have at least one colloidal dimension (1 to 100 nm).
Inter-particle spacing within an aggregation is 0.5 to 3.0 nm (avg. 1.5 nm).

H represents hexagonal crystalline products such as CH, $C_4A\bar{S}H_{18}$, C_4AH_{19}. They form large crystals, typically 1 µm wide.

C represents capillary cavities or voids which exist when the spaces orginally occupied with water do not get completely filled with the hydration products of cement.
The size of capillary voids ranges from 10 nm to 1 µm, but in well-hydrated, low water-cement ratio pastes, they are < 100 nm.

CH + S → C-S-H of low density
Pozzolanic reaction converts the denser CH phase and larger pores into less dense C-S-H and smaller pores

Fig. 6.3 — Diagrammatic representation of a well-hydrated portland cement paste (top) and a portland–pozzolan cement paste (bottom)

7. SPECIFICATIONS AND TEST METHODS

According to ASTM C 618, natural pozzolans in raw or calcinated state, are designated as Class N pozzolans. For use as a portland cement additive or as a mineral admixture in portland cement concrete, pozzolanic materials are required to meet certain chemical and physical requirements.

Chemical Requirements

The most useful chemical requirements that are contained in many standard specifications of the world, such as the Canadian CAN 3-A 23.5 and the ASTM C 618, are those requiring a maximum limit of 10% on ignition loss and 3% on free moisture. The objective of these requirements is to ensure that the pozzolan is in a dry and suitably calcined state before use.

The most controversial chemical requirement in ASTM C 618 is the one prescribing that the sum of the three principal oxides (i.e., $SiO_2 + Al_2O_3 + Fe_2O_3$) must be more than 70%. When present in a non-crystalline (glassy) or poorly crystalline state, these constituents participate in pozzolanic activity reactions. The ASTM C 618 minimum requirement on the sum of SiO_2, Al_2O_3, and Fe_2O_3, assumes that in a pozzolan these oxides are always present in a reactive form, which is seldom correct. Most natural pozzolans contain substantial amounts of quartz and feldspar, which are highly crystalline and are non-reactive to lime. Commenting on the ASTM C 618 requirement on the content of $SiO_2 + Al_2O_3 + Fe_2O_3$, Lea (1) says:

> "These overall composition requirements do not appear in European specifications and indeed the U.S. minimum requirements come close to rejecting some of the Roman pozzolans. It cannot be said that such overall limitations on composition have much practical value, and they can be unnecessarily restrictive."

Attempts have often been made to determine, by acid and alkali leaching, the content of active constituents in a pozzolan, and much of the work has been summarized by Lea (1). Extraction with hot or cold hydrochloric acid or nitric acid, or with alkali hydroxide and carbonate solutions have failed to reveal any relationship between the acid- or alkali-soluble material and the strength contribution potential of a pozzolan in a portland cement mortar or concrete.

Some specifications require determination of the pozzolanic activity from chemical tests on the lime-fixation capacity of the pozzolan. Only in some cases a close relationship has been found between the lime-fixation capacity of the pozzolan and the strength of a standard mortar made with the portland–pozzolan cement. Many researchers, including Massazza (21) and Takemoto and Uchikawa (14), have concluded that there is no relationship in the data from the two tests. Because the strength of a mortar is directly attributable to the microstructure of the hydrated cement paste present (i.e., the intrinsic strength of the hydration product and the pore-size distribution of the system), Regourd et al. (22) point out that the microstructures in the cases of two pozzolans with a similar lime-fixation capacity may not be the same.

Physical Requirements

From the standpoint of a simple method for quality control on pozzolanic activity, a test and a specification for the maximum permissible amount of coarse particles in a pozzolan is useful. ASTM C 618 limits the 325-mesh sieve residue (>45 μm) to 34%; some others prefer a lower limit, such as the Indian Standard IS-1344, which permits a maximum of 12% particles only above 45 μm.

Particle size is only one parameter controlling the pozzolanic activity; others are the composition and amount of reactive constituents such as glass, which is difficult to determine. Most standard specifications, therefore, require a direct test for the pozzolanic activity and a minimum value of the activity index. Typically, this test involves the determination of compressive strength of a test mortar containing either a lime–pozzolan or a portland cement–pozzolan mixture of specified proportions and cured under given conditions. Because of the variable quality of lime and its effect on the test results, many investigators do not favor the lime–pozzolan test.

In the ASTM C 311 pozzolanic activity test with portland cement, the test mortar contains 35% cement replacement (by volume) by the pozzolan. The water-to-cement ratio of the test mortar is not fixed, but is variable and is determined by a standard consistency test, which is an objectionable feature of the ASTM C 311 pozzolanic activity test method. Strength of a cement depends on the initial porosity (i.e., water-to-cement ratio), and the degree of pore space filled by the hydration products. If different water-to-cement ratios have been used for testing the pozzolanic activity of two pozzolans, then the strength data corresponding to a given degree of hydration would not give a true index of their pozzolanic activity because the strength is also affected by the initial porosity.

Most natural pozzolans tend to increase the water requirement in the standard consistency test as a result of their microporous character and high surface area. Most standard specifications contain an arbitrary limit on the maximum water requirement. Such arbitrary limits can be unduly restrictive because an excessive water requirement may be corrected by the application of a water-reducing agent (23).

The ASTM C 618 also contains a specification for soundness which is based on a test method involving the exposure of the portland cement–pozzolan paste to high temperature and pressure in an autoclave. This method was originally developed for the evaluation of soundness of portland cement containing undesirably large amounts of crystalline MgO or CaO. Natural pozzolans contain neither of the expansive oxides, and, therefore, comply well with the requirements of the soundness test and the specification. However, it is generally agreed that the soundness test and specification are of no value and should be deleted from the standards.

8. PROPERTIES OF CONCRETE CONTAINING NATURAL POZZOLANS

Modifications in properties of portland cement concrete as a result of addition of a pozzolan include slower rate of setting and hardening, higher ultimate strength, lower heat of hydration, and better performance in acidic environments. Clearly, these technical advantages from the use of pozzolans in concrete are not limited to natural pozzolans; they can also be obtained from the use of industrial by-products such as fly ash. However, only natural pozzolans fall within the scope of this chapter.

Setting Time

The addition of a natural pozzolan to portland cement results in set retardation partly because of the dilution effect (i.e., the dilution of the most active ingredient, which is portland cement) and partly because of the increased water requirement for making the cement paste of normal consistency. For instance, Nicolaidis (24) reported that, compared to the setting times for neat portland cement, both the initial and final setting times of a blended portland cement containing 20% Santorin earth were increased by 20 min. The water requirements to produce a paste of normal consistency were 24.5 and 26.5% for the portland cement and the blended portland cement, respectively.

Bleeding

Many investigators have observed that with blended portland cements containing pozzolans, the rate of bleeding is reduced considerably. For example, using the ASTM Method C 243-55, Nicolaidis (24) found bleeding rates of 127×10^{-6} and 84×10^{-6} cm^3/cm^2 per sec. for the portland cement and the portland–pozzolan cement (containing 20% Santorin earth), respectively. Even more impressive a reduction in bleeding was obtained by Davis and Klein (17) who used finely ground diatomite from Lompoc (California) in a lean concrete mixture. The one-hour bleeding in the reference concrete (without the diatomite) amounted to 22% of total water present. When 11% of the cement by weight was replaced with the diatomite, the bleed water was only 2% of the total water.

The reduction in bleeding results partly from the interference provided by the finely pulverized particles of the pozzolan to the water flow channels in a freshly consolidated concrete mixture and partly from the microporous character of the pozzolanic materials. It is believed now that the control of internal bleeding in concrete plays an important role in determining the strength of the transition zone between aggregate and cement paste and, therefore, the mechanical properties of concrete (25).

It should be noted that the water-retention characteristic of natural pozzolans, such as volcanic ashes and calcined clays, distinguishes them from by-product pozzolans, such as fly ash. Incorporation of the former tends to increase the water requirement of concrete whereas incorporation of the latter generally has a water-reducing effect. *The higher water-to-cement ratio of a concrete mixture containing a natural pozzolan may not necessarily impair the strength because a part of the mixing water will be adsorbed by the pozzolan and, thus, will not cause a corresponding increase in the porosity of the hardened concrete. According to Nicolaidis (24), this adsorbed water would later be available for the pozzolanic reaction.*

Heat of Hydration

Using a natural pozzolan from Italy, Massazza and Costa (13) showed that the addition of the pozzolan to a portland cement clearly reduced the heat of hydration (Fig. 8.1), however, this reduction was not directly proportional to the amount of cement replaced. It was smaller because of some evolution of heat during the pozzolanic reaction. For example, at the 20% level of cement replacement, the 90-day heat of hydration of the portland cement was reduced from 94 to 85 cal/g and the 28-day heat of hydration was reduced from 85 to 76 cal/g. Similarly, with 20% cement replacement by Santorin earth in the case of a Greek portland cement, Nicolaidis (24) found that the seven-day heat of hydration was reduced by 9 cal/g.

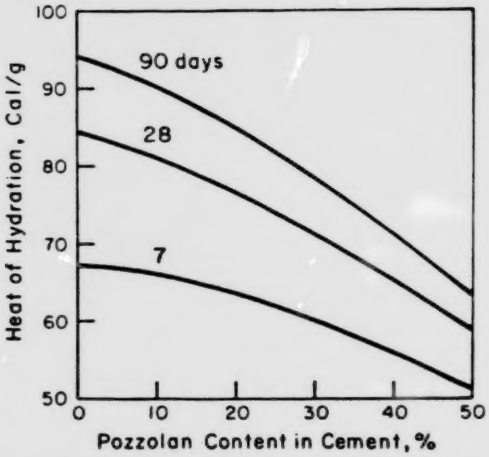


Fig. 8.1—Effect of substituting an Italian natural pozzolan on the heat of hydration of cement (13)

The ability of the pozzolanic materials to reduce the heat of hydration in portland–pozzolan cements is widely exploited in the construction of mass concrete structures, where the risk of thermal cracking can be a major problem. For this purpose, as described earlier, natural pozzolans were used first in the *United States from 1910 to 1912 for the construction of Los Angeles Aqueduct* and later in the construction of the San Francisco Bay and Golden Gate bridges, and the Friant, Bonneville, Davis, Glen Canyon, Flaming Gorge, Wanapum, and John Day dams (9).

Strength

Although the pozzolanic reactions in a portland–pozzolan cement paste begin as soon as alkalis and calcium ions are released during the hydration of portland cement, most of the pozzolanic activity and, therefore, the strength development associated with it seems to occur after seven days of hydration. Typical results from an investigation on the effect of curing time on the compressive strength of ASTM C 109 mortars made with portland–pozzolan cements containing 10, 20, or 30% Santorin earth, are presented in Figure 8.2 and 8.3.

From the compressive strength data for 1, 3, 7, and 28 days (see Fig. 8.2), it is evident that up to seven days, the strength was almost proportional to the amount of portland cement present in the blended cement. This result shows that in seven days of hydration the pozzolanic reaction had not progressed far enough to influence the strength. At 28 days, however, the strength of the

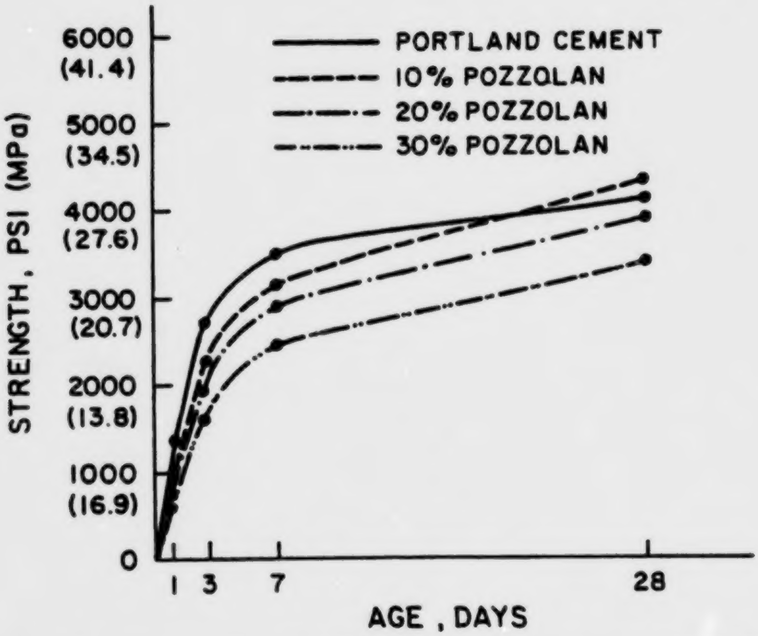


Fig. 8.2 — Compressive strengths up to 28 days of cements made with Santorin earth (12)

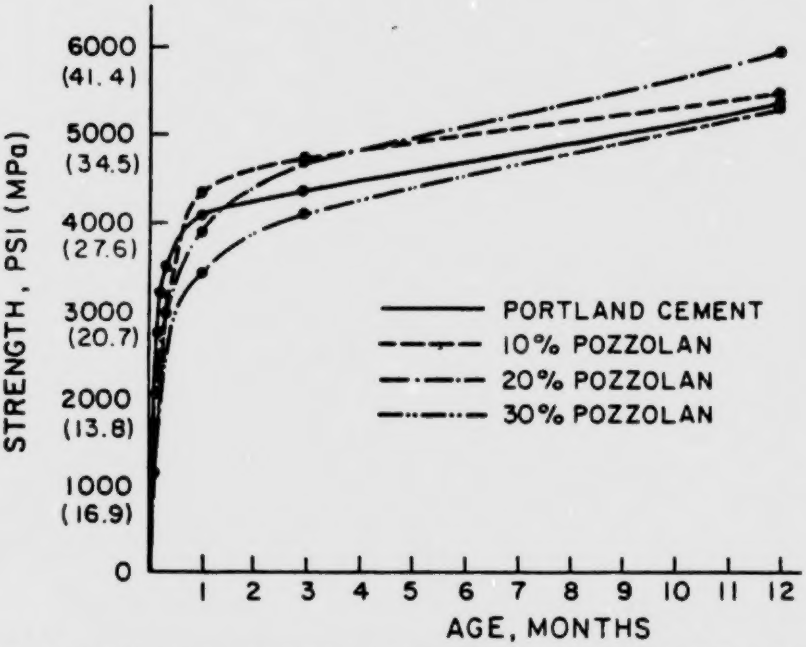


***Fig. 8.3* — Compressive strengths up to 12 months of cements made with Santorin earth (12)**

cement containing 10% pozzolan was slightly higher than the reference portland cement; the cements containing 20 and 30% pozzolan showed 7 and 18% lower strengths than the control, respectively. It was concluded from the data in Figure 8.2 that during the 7- to 28-day hydration period, the beneficial effect on strength resulting from the pozzolanic reaction was not considerable.

The data for 28- and 90-day, and one-year period in Figure 8.3 shows that at 90 days the strengths of cements with both 10 and 20% Santorin earth cements were about 10% greater than the reference portland cement. The one-year strength of the 30% pozzolan cement was similar to the reference portland cement whereas the other two pozzolan cements showed higher strengths than the reference cement. In Figure 8.4, similar results on the effect of substituting portland cement with an Italian natural pozzolan were reported by Massazza and Costa (13). The authors confirmed the slow reaction between lime and pozzolan and concluded that at early ages, the cements containing pozzolans show lower strengths than the reference portland cement; however, the ultimate strength can be higher depending on the quality and quantity of the pozzolan used. It seems that an excess of pozzolan, i.e., more than 30% by weight in the blended cement, should be avoided when a substantial reduction in the mechanical strength of the product cannot be tolerated, especially at early ages and under cold weather conditions.

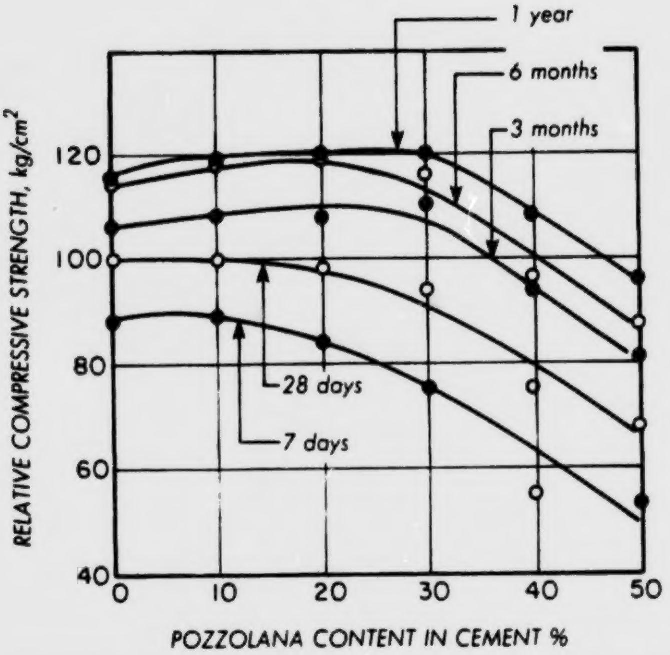


Fig. 8.4—Effect of substituting an Italian natural pozzolan for portland cement on the compressive strength of ISO mortar (13)

Durability to Sulphate Attack

The sulphate attack in concrete generally involves expansion, cracking, and loss of mechanical strength due to the formation of ettringite and gypsum. These minerals are formed as a result of interaction between a sulphate water and cement hydration products, such as the monolsulphate hydrate ($C_4A\bar{S}H_{18}$) and calcium hydroxide (CH). Sea water and ground waters from alkaline soils are the common sources of sulphate in natural waters.

It is well known that the use of natural pozzolans, in the form of cementitious lime–pozzolan or portland cement–pozzolan mixtures, has a beneficial effect on the durability of concrete exposed to sulphate water. This durability is because the pozzolanic reactions not only reduce the permeability of concrete but also result in the formation of a sulphate-resisting product (i.e., less calcium hydroxide present in the hydrated cement paste, and CSH with lower CaO-to-SiO_2 ratio). The results from numerous laboratory investigations including those discussed later seem to confirm that the addition of a natural pozzolan enhances the resistance of portland cement to sulphate attack.

Massazza and Costa (13) reported the effect of substituting portland cement with 10, 30, and 40% of an Italian pozzolan on the expansion of 1:3 mortar prisms stored for more than five years in a 1% $MgSO_4$ solution (Fig. 8.5). With the mortars containing 30 or 40% cement replacement by the pozzolan, the expansion was considerably reduced. The authors attributed the results to the reduced content of calcium hydroxide and to higher impermeability. According to them, the free calcium hydroxide in hydrated pozzolan cements would not only be present in a lower amount but it would also be surrounded by impermeable CSH gel. These conditions are unfavorable to the formation of ettringite, which is generally considered to be the agent causing expansion and cracking.

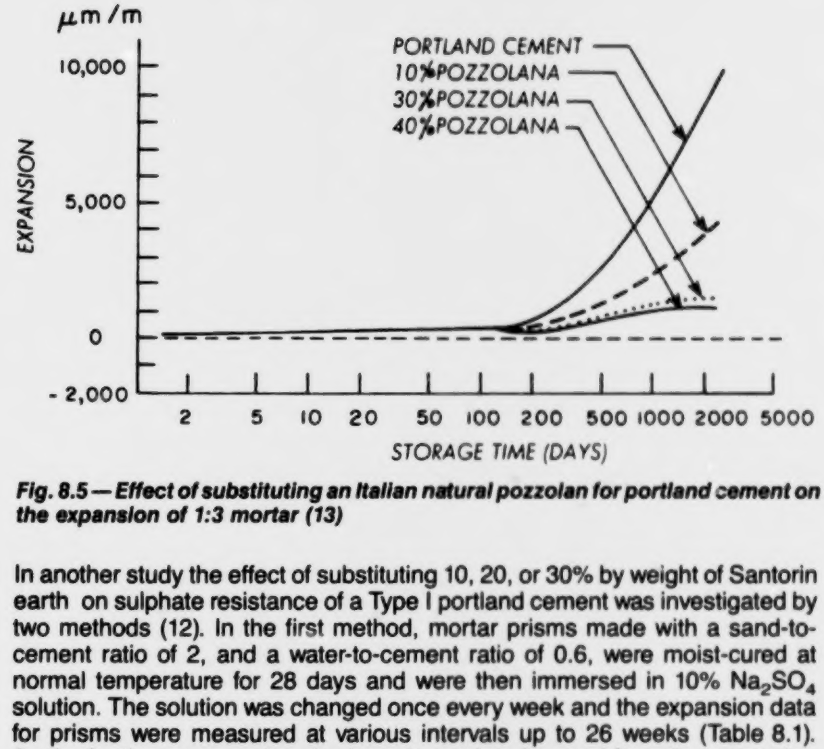


Fig. 8.5 — Effect of substituting an Italian natural pozzolan for portland cement on the expansion of 1:3 mortar (13)

In another study the effect of substituting 10, 20, or 30% by weight of Santorin earth on sulphate resistance of a Type I portland cement was investigated by two methods (12). In the first method, mortar prisms made with a sand-to-cement ratio of 2, and a water-to-cement ratio of 0.6, were moist-cured at normal temperature for 28 days and were then immersed in 10% Na_2SO_4 solution. The solution was changed once every week and the expansion data for prisms were measured at various intervals up to 26 weeks (Table 8.1). Again, for the reasons already given, it may be observed from the expansion data that the sulphate attack was considerably less severe on the mortars made with 20 or 30% pozzolan cements.

The second test for sulphate resistance of the blended portland cements containing Santorin earth involved an accelerated method (26). According to this test, the criterion for sulphate resistance is the relative loss in compressive strength when specimens of neat cement paste are immersed in a 4% Na_2SO_4 solution, which is maintained at a constant pH and sulphate concentration. Before immersion in the sulphate, the specimens were subjected to accelerated curing at 50°C for seven days. In this test the cements showing 25% or

Table 8.1 — Expansion of mortar prisms in sulphate solution*

Cement type	Expansion, %			
	4 weeks	8 weeks	12 weeks	26 weeks
Portland cement	0.004	0.034	0.212	0.520
10% Santorin earth	0.006	0.018	0.071	0.285
20% Santorin earth	0.007	0.010	0.048	0.050
30% Santorin earth	0.006	0.008	0.027	0.050

*Reference 12.

higher strength loss in 28 days of sulphate exposure are presumed to perform unsatisfactorily. Again, the test data shown in Table 8.2 confirmed the conclusion from the first test that cements containing 20 or 30% Santorin earth were resistant to sulphate attack. Whereas the reference portland cement and the cement containing 10% Santorin earth lost more than 50% strength as a result of sulphate immersion, those containing 20 or 30% Santorin earth did not lose more than 20% strength.

Table 8.2 — Compressive strength loss of cement paste cylinders in sulphate solution held at constant pH*

Cement type	Strength before immersion, MPa	Strength after 28 days immersion, MPa	Strength loss
Portland cement	18.0	6.1	65%
10% Santorin earth	18.5	9.5	49%
20% Santorin earth	16.1	12.9	20%
30% Santorin earth	15.2	12.8	16%

*Reference 12.

Studies by Davis et al. (27) regarding the influence of various natural pozzolans from California on the resistance of the cement to the action of a sodium sulphate solution showed why some pozzolan types are useful in combating the sulphate attack whereas others are not. Blended portland cements containing crystalline silicas, granite, and quartz reduced the sulphate resistance of the cement, however, cements containing reactive silica, such as Monterey shale, diatomaceous earth, and pumicite, improved the resistance of the cement to sulphate attack. This finding confirms the earlier analysis that only those materials that are capable of entering into pozzolanic reaction with lime can be relied upon to offer the technical advantages normally associated with their use in concrete.

Resistance to Alkali–Silica Expansion

The chemical interaction of certain siliceous mineral constituents of aggregate with the alkalis in portland cement is known to cause expansion and cracking of concrete. The commonly practised method of reducing the risk of such expansion involves the use of a low-alkali cement. Alternatively, where possible, the reactive aggregate source is replaced by a non-reactive source. When the use of a high-alkali portland cement (>0.6% Na_2O equivalent) in combination with an aggregate containing alkali-reactive constituents seems unavoidable, the expansion phenomenon may be controlled by incorporating into the concrete mixture a pozzolanic material that has proven in laboratory tests to be effective in reducing the alkali–aggregate expansion.

The mechanisms by which the alkali–silica reaction in concrete is able to cause expansion and the use of a pozzolanic material reduces the expansion, are not fully understood. Some researchers assume that the expansion and cracking are caused by the osmotic pressure when the alkali–silicate gels imbibe large amounts of water. Thus, it is suggested that, depending upon the particle size, reactivity, and the amount of pozzolan added, the alkali–silica gel may be evenly distributed throughout the concrete with the result that there is no opportunity for the formation of a large mass of gel that would cause sufficient localized osmotic pressure to rupture the concrete (28,29). Others believe that, in the presence of pozzolans, instead of alkali–silica gels, alkali–lime–silicates of low alkali-to-silica ratio are formed, which have only slight solubility.

Regardless of the mechanism by which the expansion associated with the alkali–silica reaction is controlled by the incorporation of a pozzolan in concrete, it has been observed by many investigators that natural pozzolans are found to be more efficient for this purpose than by-product pozzolanic materials. For instance, Pepper and Mather (30) found that the percentage by solid volume of the pozzolan needed to replace portland cement for adequate reduction of expansion (as required to meet the requirements of the ASTM C 441) varied from 20% with diatomite, 20 to 30% with calcined shale, and 40 to 50% with fly ash.

All natural pozzolans are not equally effective in combating alkali–silica expansion. Pepper and Mather (30) reported that in the case of a volcanic glass, cement replacement in the order of 30 to 35% was needed to meet the requirements of the ASTM C 441. Similarly, using an accelerated test procedure (31), the results of an investigation showed (Fig. 8.6) that a portland cement (1.0% equivalent Na_2O), blended with 20 or 30% Santorin earth was quite satisfactory with regard to control of the alkali–silica expansion. It may be pointed out here that many natural pozzolans themselves contain a high alkali content. For instance, the chemical analysis of the Santorin earth (see Table 3.1) shows 3.9% Na_2O and 2.6% K_2O (5.6% Na_2O equivalent). It seems that under normal conditions in concrete *the alkali ions, bound in the framework-type crystal structure of feldspar or mica, are not released and, therefore, do not play any deleterious role in the alkali–silica expansion.*

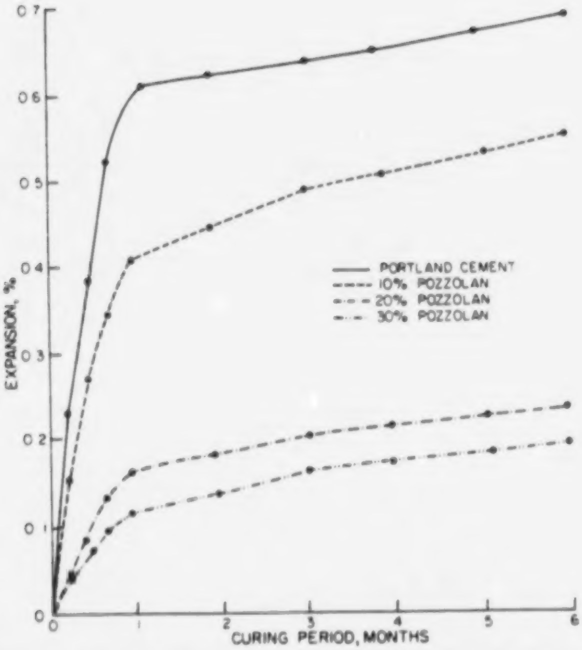


Fig. 8.6 — Control of alkali–silica expansion by Santorin earth (12)

Durability to Frost Action

Incorporation of natural pozzolans does not impair the freezing and thawing durability of a concrete provided it has been adequately protected by air-entrainment. Finely ground pozzolans tend to reduce the amount of entrained air in a concrete mixture and, therefore, may require a higher-than-normal dosage of the air-entraining admixtures to obtain a given amount of entrained air or the desired spacing factor.

Drying Shrinkage

The drying shrinkage of products made with portland–pozzolan cements is generally higher than that of the corresponding product containing portland cement alone. This difference is to be expected because the drying shrinkage of a hydrated cement paste is generally attributable to the content of CSH, which would be relatively more in the case of portland–pozzolan cements. However, many researchers have observed that the *cracking tendency resulting from drying shrinkage in concretes containing pozzolans is less than that in corresponding concretes without pozzolans*.

There are probably two explanations as to why the incidence of drying shrinkage cracking in portland–pozzolan cement products is not as high as expected. First, it seems that the restraining effect of aggregate on the shrinkage of the cement paste in mortar or concrete plays a more important part in determining the total amount of the shrinkage. In a 90-day shrinkage test with mortar prisms, Massazza and Costa (13) found that compared to 890 μm/m for ordinary portland cement, the drying shrinkage of the cement containing an Italian pozzolan was only 943 μm/m. In another study using concrete prisms and an 80-week drying period (12), it was found that compared to the reference portland cement, the drying shrinkages of concretes made with blended cements containing 10, 20, or 30% Santorin earth were not significantly different (Fig. 8.7).

The second explanation for relatively less cracking in portland–pozzolan cement products lies probably in the stronger transition zone between the aggregate and cement paste, compared to a corresponding concrete (with similar water-to-cement ratio) without the pozzolan. Therefore, at a given ratio of water to the cementitious material, the flexural and tensile strengths of portland–pozzolan cement concrete tend to be higher than the pozzolan cement concrete. This increases the tensile strain capacity and hence the crack resistance of the former under given shrinkage conditions.

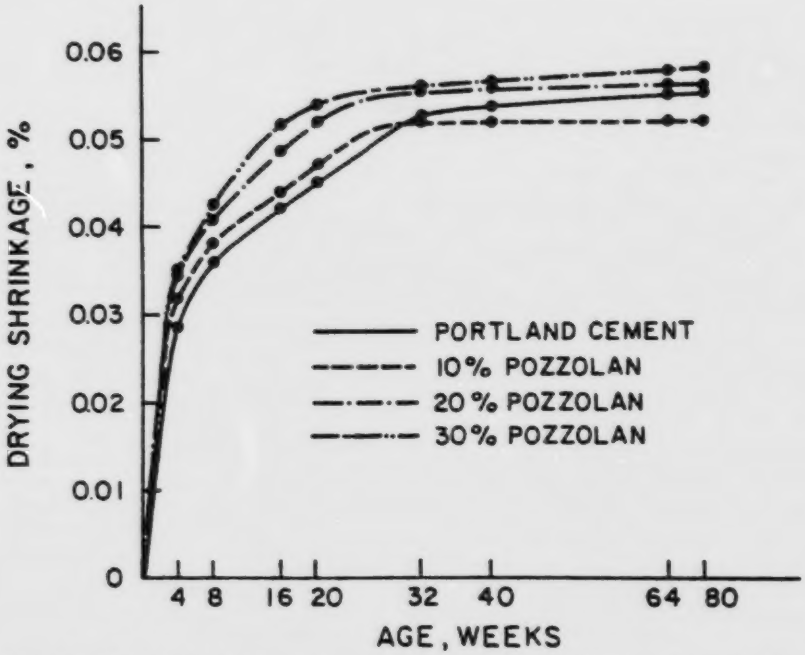


Fig. 8.7 — Drying shrinkage of concrete prisms made with cements containing various amounts of Santorin earth (12)

9. THE USE OF NATURAL POZZOLANS IN THE FUTURE

When properly employed as an ingredient of portland–pozzolan cements or as admixtures to portland cement concrete, pozzolans can improve the performance of both fresh and hardened concrete. In fact, some of the technical advantages made possible by the use of pozzolans in concrete are unattainable when ordinary portland cement is used alone. The advantages include improvement in workability, reduction in heat of hydration, increase in watertightness and ultimate strength, and enhanced resistance to sulphate attack and to alkali–aggregate expansion. In addition, the use of pozzolans in concrete is frequently cost-effective and energy-saving.

Industrial by-products, such as fly ash and condensed silica fume, are finding increasing use as pozzolans, because they are plentiful in many parts of the world and, unlike natural pozzolans, they usually do not require any pulverization or heat treatment before use. However, in several countries, such as China, Greece, Italy, India, and Mexico, millions of tons of natural pozzolans are still being used for making blended portland cements. For reasons of economy and energy-saving, their use is expected to continue, or even to increase, in the future.

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CHAPTER 2

FLY ASH IN CONCRETE

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1. INTRODUCTION

Fly ash is a by-product of the combustion of pulverized coal in thermal power plants. It is removed by the dust collection system as a fine particulate residue from the combustion gases before they are discharged into the atmosphere.

Fly ash particles are typically spherical, ranging in diameter from less than 1 to more than 150 μm, the majority being less than 45 μm. The range of particle sizes in any given fly ash is largely determined by the type of dust collection equipment used. The fly ash from boilers at some older plants, where mechanical collectors alone are employed, is coarser than from plants using electrostatic precipitators.

The chemical composition of fly ash is determined by the types and relative amounts of incombustible matter in the coal used. More than 85% of most fly ashes comprise chemical compounds and glasses formed from the elements silicon, aluminum, iron, calcium, and magnesium. Generally, fly ash from the combustion of subbituminous coals contains more calcium and less iron than fly ash from bituminous coal. Unburned coal collects with the fly ash as carbon particles, the amount being determined by such factors as the rate of combustion, air/fuel ratio, and degree of pulverization of the coal. In general, fly ash from subbituminous coals contains very little unburned carbon. Plants that operate only intermittently (peak load stations), burning bituminous coals, produce the largest percentage of unburned carbon.

Fly ashes exhibit pozzolanic activity. A pozzolan is defined (1) as "a siliceous or siliceous and aluminous material which in itself possesses little or no cementitious value but which will, in finely divided form and in the presence of moisture, chemically react with calcium hydroxide at ordinary temperature to form compounds possessing cementitious properties." Fly ashes contain meta-stable alumino-silicates that will react with calcium ions, in the presence of moisture, to form calcium silicate hydrates.

The term *fly ash* was coined in the electrical power industry in about 1930. The first comprehensive data on its use in concrete in North America were reported in 1937 by Davis et al. (2). The first major practical application was reported in 1948 with the publication by the United States Bureau of Reclamation of data on the use of fly ash in the construction of the Hungry Horse Dam. Worldwide acceptance has followed slowly upon these early efforts, and its growth has been particularly noticeable in the wake of the rapid increase in energy costs (and hence cement costs) that occurred during the 1970's.

In 1977, Manz (3) reported the estimated production of coal ash, worldwide, to be 278 443 000 metric tons of which approximately 11.4% was used. Table 1.1 shows the estimated percentage of the collected fly ash used in cement and concrete in eight countries as reported in 1982 by Idorn (4).

Table 1.1 — Percentage of collected fly ash used in cement and concrete in eight countries*

Country	% Used	Year
France	24	1978
U.K.	19	1978
Poland	14	1975
Denmark	14	1981
W. Germany	8–10	1978
Canada**	7	1982
United States	6	1978
India	1	1978

*From reference 4.

**Data for Canada revised to reflect recent usage.

The inclusion of fly ash in concrete affects all aspects of concrete properties. As a part of the composite that forms the concrete mass, fly ash acts in part as fine aggregate and in part as a cementitious component. It influences the rheological properties of the fresh concrete, the strength, finish, porosity, and durability of the hardened mass, and the cost and energy consumed in manufacturing the final product.

In recent years, there has been a recognition that fly ashes differ in significant and definable terms, reflecting their composition and, to some extent, their origin. Canadian (5) and U.S. (6) specifications recognize two general classes of fly ash:

- — Class C, normally produced from lignite or subbituminous coals;
- — Class F, normally produced from bituminous coals.

The Class C ashes differ from the Class F materials principally in often having a capacity for self-hardening in the absence of cement. The most notable chemical difference between these two classes of ash is that the Class C ashes contain high levels of calcium that has led to the use of an alternative, and in some ways preferable, terminology: high-calcium and low-calcium ash for Classes C and F, respectively. This terminology has been adopted where appropriate throughout this review. It should be noted that this distinction has not been made in the applicable North American specifications. These at present make no reference to CaO content.

A previous review of the use of fly ash in concrete was published by Berry and Malhotra (7) covering the period from 1960 to 1978. Many significant developments have been reported since then. A number of conferences and seminars of international scope have been held (8–15) and numerous research papers and accounts of fly ash utilization in construction projects have been published.

Wherever possible, while remaining consistent with a critical overview of the subject, emphasis in this chapter has been placed on recently published material not included in earlier literature reviews by Abdun-Nur (16), Jarriage (17), Snyder (18), Kokubu (19), and Rosner and Hamm (20), each of which remains a valuable source of published material. In some instances, material cited and discussed in the previous review (7) has been omitted or replaced with newer information in an endeavour to present material that is as relevant as possible to the current use of fly ash in concrete.

2. PROPORTIONING CONCRETES CONTAINING FLY ASH

In most applications, the objective in using fly ash in concrete is to achieve one or more of the following benefits:

- — reducing the cement content to reduce costs;
- — obtaining reduced heat of hydration;
- — improving workability;
- — attaining required levels of strength in concrete at ages beyond 90 days.

In practice, fly ash can be introduced into concrete in one of two ways:

- — A blended cement containing fly ash may be used in place of portland cement.
- — Fly ash may be introduced as an additional component at the concrete-mixing plant.

The first method is the simpler; it is free from the complications of batching additional materials and more uniform control may be assured. The relative proportions of fly ash and cement are predetermined and, thus, the range of mix proportions is effectively limited.

The second method is flexible and allows for more complete exploitation of the qualities of fly ash as a component of concrete. It does, however, demand that the unique properties of fly ash be considered in determining the mix proportions. The present trend in North American practice is towards the use of fly ash as a separately batched concrete material.

Fly ash plays more than one role in concrete. In the freshly mixed state, it generally acts as a fine aggregate and to some degree may reduce water demand. In the hardened state, because of its pozzolanic nature, it becomes a component of the cementitious matrix and influences strength and durability. Thus, using fly ash in a concrete introduces a number of complexities with regard to proportioning if the accepted relationships between workability, strength, and water–cement ratio are employed.

Two common assumptions are made in selecting an approach to mix proportioning fly ash concrete:

— Fly ash usually reduces the strength of concrete at early ages.

— For equal workability, concrete incorporating fly ash usually requires less water than concrete containing only portland cement.

Neither assumption is universally true and both are influenced by the presence of other commonly used concrete components. However, both assumptions have strongly influenced the ways in which the problem of proportioning concrete mixes to incorporate fly ash has been approached.

Throughout the more than 40 years during which fly ash has been used in concrete, it has been the more common practice to refer the mix proportions of fly ash concretes to some reference plain concrete. Similarly, the properties in both the fresh and hardened conditions were usually compared with a reference concrete. Thus, fly ash was generally thought of as replacing cement rather than being a component that complements the functions of other components, in particular the cement, sand, and water. Recently, there has been a trend to consider the components of fly ash concrete as a whole and to treat it as a unique material without reference to an "equivalent plain concrete mix." As a consequence of these different ways of thinking about fly ash in concrete, three basic mix-proportioning methods have developed:

— partial replacement of cement — the Simple Replacement Method;

— addition of fly ash as fine aggregate — the Addition Method;

— partial replacement of cement, fine aggregate, and water —

a) the Modified Replacement Method;

b) the Rational Proportioning Method.

Simple Replacement Method

The Simple Replacement Method requires a direct replacement of a portion of the portland cement by fly ash (21). Much research has shown that any percentage replacement of portland cement in concrete by fly ash on a one-for-one basis (either by volume or by mass) results in lower compressive and flexural strengths up to about three months of moist curing, with the development of greater strengths beyond six months. In mass-concrete applications, where fly ash first came into use, this reduced early strength was of little structural consequence when considered in the light of the desired reduction in temperature rise; replacement methods of mix proportioning were generally used.

The general form of strength development in fly ash concrete when partial replacement of cement is used, is shown graphically in Figure 2.1. The general behaviour of the system is consistent with the view that at early ages fly ash exhibits very little *cementing value* and acts rather as a fine aggregate; at later ages cementing activity becomes apparent and a considerable contribution to strength may result. In this regard, high-calcium fly ashes differ greatly from low-calcium ashes, as is discussed in some detail in Section 4 of this chapter.

Addition Method

In the Addition Method, fly ash is added to the mix without a corresponding reduction in the quantity of cement used. The effective cementitious content of the concrete (especially after long periods of moist-curing) is increased by this method. Other mix adjustments are usually made through changes in aggregate content and depend on the nature of the particular job.

An example of this approach comes from the investigation of concrete materials for the construction of the South Saskatchewan River Dam made by Price (22). For reasons of sulphate resistance, it was considered important to use a minimum cement factor and to use pozzolan as a replacement for fine aggregate rather than for cement. It was found that addition of fly ash generally produced increased strength in concrete at all ages. Improvements were small at seven days but ranged up to 6.9 MPa at three months and one year. In some cases, improvements were equal to, or greater than, those obtained by an equal addition of cement. In contrast to fly ash, the addition of pumicite resulted in reduced strengths at all ages.

The third method developed for proportioning fly ash concrete requires a part of the cement to be replaced with an excess by mass of fly ash, with adjustments made in fine aggregate and water content. The method has two variants. In its original form, it has been termed the Modified Replacement Method; in recent practice developments have led to so-called Rational Proportioning Methods.

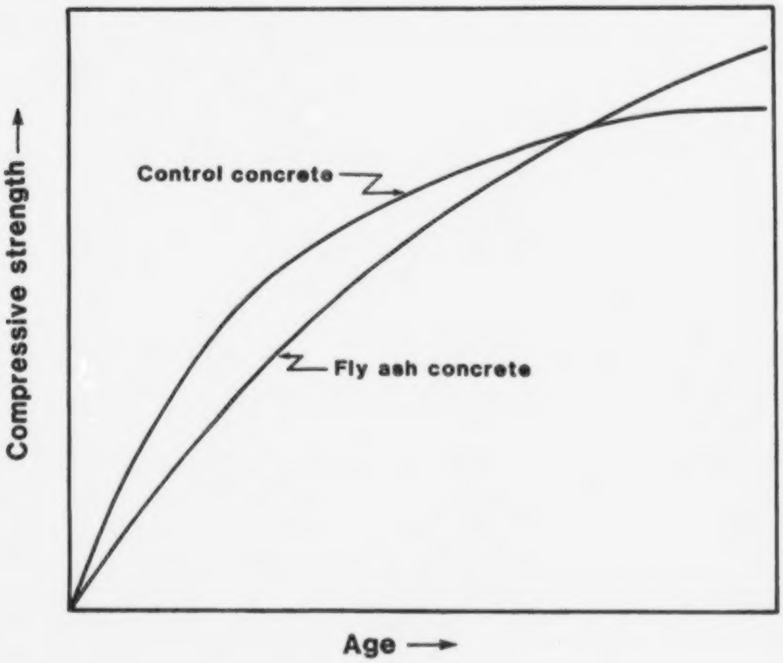

Fig. 2.1 — Relative rates of strength increase of plain concrete and fly ash concrete proportioned by simple replacement of cement

Modified Replacement Method

The Modified Replacement Method probably originated in 1958 with the work of Lovewell and Washa (23) who showed that by modification of mix proportions, fly ash concretes could be made that had strengths at early ages comparable with those of control mixes.

The main point of their conclusions was:

> *"In order to obtain approximately equal compressive strengths at early ages, between 3 and 28 days, mixes made with fly ash must have a total weight of portland cement and fly ash greater than the weight of the cement used in the comparable strength portland cement mixes."*

In the early 1960's it was realized that, if fly ash concrete were to comply with the normally specified requirements of workability and strength, then the characteristics of fly ash most affecting those properties must be accounted for in proportioning mixes. This realization has resulted in the development of several methods of proportioning that are based upon Abrams' relationship (24) between strength and water-to-cement ratio.

Rational Proportioning Method

Smith (25) was probably the first to propose a rational method of proportioning fly ash concrete. He modified the conventional mix-proportioning procedure to obtain values for cement content and water-to-cement ratio through the introduction of a "fly ash cementing efficiency factor" (k). This factor was assumed to be unique for each fly ash and could be determined from the performance of fly ash concrete mixes or from an initial testing program.

The cementing efficiency factor was defined such that a mass of fly ash (F) was equivalent to a mass (kF) of cement. The required strength and workability of fly ash concrete are then considered to be controlled by the volume ratios of cement-sized particles to water and aggregate, and by the relationship between strength and the ratio of water content to total *cementing material*: $W/(C+kF)$.

The method was applied in Britain, and charts were prepared to simplify proportioning procedures (26). However, as Munday et al. (27) have noted, the approach has certain weaknesses in practice.

1. The value for k is not constant for any particular fly ash. It varies depending upon the cement used (28), the curing conditions employed (29,30), and the nominal strength level to which the concrete is being proportioned (31).
2. The differences in water demand between cement and fly ash and between different fly ashes, cause adjustments to be required to the aggregate content to achieve the desired workability. This was considered to be impractical because, in construction practice, water content is usually adjusted, thus increasing the variability of the strengths attained.
3. The method is complex and probably impractical for most purposes.

Attempts to develop proportioning methods for fly ash concrete based upon Abrams' relationship have been proposed by a number of authors in the context of North American concrete practice.

In 1968, Cannon (32) reported research carried out by the Tennessee Valley Authority on methods of proportioning fly ash concrete mixes to obtain strengths at 28 and 90 days equal to those of conventional control mixes. Cannon employed Abrams' relationship between water-to-cement ratio and strength, and introduced a factor that took account of the relative costs of fly ash and portland cement. This approach, combined with extensive laboratory investigations and field experience, allowed him to develop tables and graphs to facilitate proportioning procedures.

Just as Lovewell and Washa (23) had advocated, Cannon's approach results in the use of a combined mass of portland cement and fly ash greater than the mass of the cement used in a comparable control mix. Cost savings using this method rest upon a significantly lower cost for fly ash than for portland cement.

Rosner (33) outlined a further procedure incorporating some of the concepts from Cannon (32) and from Smith (25).

In 1975, Ghosh (34) further extended the approaches developed by Lovewell and Washa, and by Cannon. Ghosh published a series of empirical relationships which considerably simplified the mix-proportioning of fly ash concrete. He extended the basic Abrams' relationship, i.e., the strength of a fully compacted concrete is inversely proportional to the water-to-cement ratio, to include the water-to-(cement + fly ash) ratio.

More recently, Popovics (35) has used data from Ghosh's work to develop empirical expressions relating strength and mix proportions for fly ash concrete.

In 1981, the American Concrete Institute published a revised "Standard Practice for Selecting Proportions for Normal, Heavyweight and Mass Concrete" (ACI 211.1-81) (36) that included guidelines for proportioning pozzolan concrete. Two approaches were taken: use of equivalent mass of cementitious material; and use of equivalent absolute volume of cementitious material. Whichever of these approaches is taken, the resulting mix is effectively proportioned by the simple replacement method.

In respect of the known behaviour of fly ash in concrete mixes, using a simple replacement approach can be expected to lead to reduced strength at least until 28 days and probably to much later ages. It is perhaps significant that the literature cited in the Report of ACI Committee 212.1R-81 (37), "Admixtures for Concrete," contains no reference to original research work published after 1968. It should be recognized that much of the early work was conducted using high-carbon, coarse particulate, Class F fly ashes from older power plants. Much of the currently available fly ash, and certainly the ash that will become available in the future as coal-burning power generation expands, comes from modern power plants with high-efficiency combustion, dust removal, and coal pulverization equipment (many burning subbituminous coals). Most of the problems experienced with the use of fly ash during the period from 1950 to 1970 will no longer be relevant to modern concrete practice.

In 1982, a National Standard was issued in Canada for supplementary cementing materials and their use in concrete construction (5). In addition to standardizing practice with regard to fly ash use in concrete, the Standard presents guidelines for proportioning fly ash concrete. The approach is based upon the method developed by Ghosh (34).

In principle, the recently introduced mix-proportioning methods discussed above have demonstrated that it is possible to proportion fly ash concretes to have strength at any desired age equal to, or in excess of, that of comparable, conventional concretes. However, a number of factors must be considered when these approaches are used in practice:

- As in a normal mix-proportioning procedure, trial mixes must be made, and the concrete components must be adjusted. Additionally, because each fly ash has unique characteristics, knowledge of each fly ash must be developed as an aid to trial mix-proportioning.
- To truly estimate the economic advantages offered by these mix-proportioning methods, allowance should be made for the handling of an extra component when fly ash is used as an admixture and batched separately. Such allowances are not made in the procedures outlined above.
- Concretes made with fly ash are more sensitive to temperature and moisture conditions during curing than are plain concretes. These factors must be considered when data from trial mixes are used to proportion concrete for construction.

3. EFFECTS OF FLY ASH ON PROPERTIES OF FRESH CONCRETE

Fresh concrete is a concentrated suspension of particulate materials, of widely differing densities, particle sizes, and chemical compositions, in a solution of lime and other components. The system is not static. As soon as the cement and water mix, reactions commence that ultimately produce the binder that consolidates the concrete mass. New particles are formed, and original particles dissolve or are coated with cementitious products. The forces of dispersion, flocculation, and gravity compete to determine the spatial distribution of the materials in the changing mass. Heat is released during the chemical reactions and the temperature rises. In all of these events fly ash plays some role. Low-calcium fly ash will act largely as a fine aggregate of spherical form, high-calcium fly ash on the other hand may participate in the early cementing reactions, in addition to being part of the particulate suspension.

Because concrete must be mixed and placed, frequently in heavily reinforced formwork, it is necessary that in most cases a level of fluidity, generally termed workability, be maintained. This is determined by the rheological properties of the system that are influenced by all the components. Control of workability is one of the objectives of mix-proportioning.

Therefore, it is essential to understand the role of fly ash in the rheology of fresh concrete if the optimum exploitation of its properties is to be made.

In practical terms, the fluidity of concrete is expressed in such phenomenological measurements as workability, compactability, pumpability, water demand, and bleeding. As the use of fly ash has increased, a gradual understanding of its role in determining these properties has started to form. This section is largely concerned with these issues and with the other important properties of fresh concrete: temperature rise and air-entrainment.

Recent work at CANMET (38) illustrates some of the effects of fly ash on the general properties of fresh concrete. The study concerned the examination of eleven fly ashes from widely different sources in Canada. The chemical and physical properties of these ashes are given in Table 3.1. A number of air-entrained concretes have been prepared using simple replacement of cement and proportioning the mixes to obtain equal ratios of water-to-(cement + fly ash) at a fixed, total cementitious materials content. Table 3.2 shows the mix proportions used and the properties of the fresh concretes obtained.

In general, it is clear that, at a fixed water-to-(cement + fly ash) ratio, slump does not always increase with the incorporation of fly ash. Another important factor revealed by this work is that the amount of air-entraining admixture required to provide 6% air varied greatly from one ash to another, and was not always in excess of the quantity required by the control concrete. Both of these issues are discussed in detail elsewhere in this section.

Table 3.1 — Properties of some Canadian fly ashes*

Fly ash source	Type of coal**	Chemical composition***, weight per cent												
		SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	Na_2O	K_2O	TiO_2	P_2O_5	MnO	BaO	SO_3	LOI****
1	B	47.1	23.0	20.4	1.21	1.17	0.54	3.16	0.85	0.16	0.78	0.07	0.67	2.88
2	B	44.1	21.4	26.8	1.95	0.99	0.56	2.32	0.80	0.27	0.12	0.07	0.96	0.70
3	B	35.5	12.5	44.7	1.89	0.63	0.10	1.75	0.56	0.59	0.12	0.04	0.75	0.75
4	B	38.3	12.8	39.7	4.49	0.43	0.14	1.54	0.59	1.54	0.20	0.04	1.34	0.88
5	B	45.1	22.2	15.7	3.77	0.91	0.58	1.52	0.98	0.32	0.32	0.12	1.40	9.72
6	B	48.0	21.5	10.6	6.72	0.96	0.56	0.86	0.91	0.26	0.36	0.21	0.52	6.89
7	SB	55.7	20.4	4.61	10.7	1.53	4.65	1.00	0.43	0.41	0.50	0.75	0.38	0.44
8	SB	55.6	23.1	3.48	12.3	1.21	1.67	0.50	0.64	0.13	0.56	0.47	0.30	0.29
9	SB	62.1	21.4	2.99	11.0	1.76	0.30	0.72	0.65	0.10	0.69	0.33	0.16	0.70
10	L	46.3	22.1	3.10	13.3	3.11	7.30	0.78	0.78	0.44	0.13	1.18	0.80	0.65
11	L	44.5	21.1	3.38	12.9	3.10	6.25	0.80	0.94	0.66	0.17	1.22	7.81	0.82

*From reference 38.

**B: Bituminous; SB: subbituminous; L: lignite.

***Inductively Coupled Argon Plasma (ICAP) Technique, except for Na_2O, K_2O, SO_3, and LOI.

****Between 105 and 750°C.

Table 3.2 — Mix proportions and properties of concretes incorporating some Canadian fly ashes*

	Batch quantities, kg/m³						Cement replacement by fly ash
			Aggregate		AFA,		%
Mix no.**	Cement	Fly ash	Fine	Coarse	mL/m³	W/(C + F)***	by mass
Control	295	0	782	1082	170	0.50	0
F1	236	59	780	1077	320	0.50	20
F2	237	59	782	1080	200	0.50	20
F3	237	59	786	1088	200	0.50	20
F4	238	59	792	1094	160	0.50	20
F5	237	59	782	1080	690	0.50	20
F6	238	59	784	1082	660	0.50	20
F7	239	59	780	1077	370	0.50	20
F8	236	59	775	1069	230	0.50	20
F9	236	59	775	1070	240	0.50	20
F10	237	59	781	1079	290	0.50	20
F11	237	59	782	1080	150	0.50	20

					Setting time, h:min	
Mix no.	Slump, mm	Air, %	Unit wt., kg/m³	Bleeding, %	Initial	Final
Control	70	6.4	2320	2.9	4:10	6:00
F1	100	6.2	2300	3.1	4:50	8:00
F2	105	6.2	2310	4.6	7:15	10:15
F3	100	6.2	2310	5.1	5:20	8:10
F4	110	6.3	2320	4.3	6:20	8:25
F5	65	6.4	2310	2.7	5:15	8:55
F6	75	6.5	2300	2.6	4:30	6:50
F7	100	6.1	2300	2.9	4:15	6:20
F8	115	6.2	2300	5.6	5:10	7:30
F9	100	6.4	2280	4.4	5:25	9:00
F10	130	6.5	2290	2.5	4:45	7:00
F11	140	6.6	2290	0.6	4:00	6:05

*From reference 38.

**Mix numbers correspond with fly ash numbers in Table 3.1.

***Water-to-(cement + fly ash) ratio by mass.

Influence of Fly Ash on the Setting Time of Portland Cement Concrete

The rate at which concrete sets during the first few hours after mixing is expressed as initial and final setting time, and is determined by some form of penetrometer test.

It may be expected that fly ash would influence the rate of hardening of cement for one or more of a number of reasons:

- The ash itself may be cementitious (high-calcium).
- Fly ash may contain sulphates that react with cement in the same way as does the gypsum added to portland cement.
- The fly ash–cement mortar may contain less water as a consequence of the presence of fly ash, and this will influence the rate of stiffening.
- The ash may absorb surface-active agents added to modify the rheology (water reducers) and again influence stiffness in the mortar.
- Fly ash particles may act as nuclei for crystallization of cement hydration products (39).

There seems to be general agreement in the literature that low-calcium fly ashes show a degree of retarding influence on cement setting. In experiments conducted at CANMET (38), the data obtained (see Table 3.2) show that all except one of the eleven ashes examined significantly increased both the initial and final setting times. Fly ashes with CaO content ranging from 1.4 to 13.0% were included in this study.

Lane and Best (40) state that fly ash generally slows the setting of concrete. They conclude that the observed retardation may be affected by the proportions, fineness, and chemical content of the ash; however, the cement fineness, the water content of the paste, and the ambient temperature are considered to have a much greater effect.

Davis et al. (2) concluded that fly ash–cement mixes set more slowly than corresponding cements, but that the setting times were within the usual specified limits.

Mailvaganam, Bhagrath, and Shaw (41) examined a number of properties of fresh and hardened concretes made at two temperatures, with a low-calcium fly ash, in the presence of various admixtures. Concretes mixed at 5°C showed retardation to give setting times in excess of 10 h, regardless of fly ash content. Concretes mixed at 20°C, and containing 30% of fly ash (by weight of cement) showed setting times extended by about 1 to 1.75 h.

Dodson (42) has sought to separate the chemical from the physical influences that fly ash might have on the setting of concrete. He observes that in concrete not containing fly ash, all conditions being equal, the setting time should be a function of two parameters:

- — the cement factor
- — the water-to-cement ratio.

As the cement factor increases, the setting time decreases; as the water-to-cement ratio increases, the setting time increases.

Dodson proposes the use of a factor (which he terms the Omega Index Factor (OIF)) expressing the combined influence of these two parameters in the form:

$$\text{OIF} = \frac{\text{cement factor}}{\text{water-to-cement ratio}}$$

Dodson reported setting time determinations for 19 concrete mixes, of which four contained low-calcium fly ashes, one contained high-calcium fly ash, and cements of three different origins were used.

The following conclusions can be drawn from this work:

- — Initial and final setting times are influenced by the water-to-cement ratio and the total cement content of the concrete. The effects can be represented by a relationship to OIF.
- — The relationship between setting times and OIF of concretes made from different cements, while each following the same general form, differs from one another considerably.
- — Whereas measured setting times for concretes containing low-calcium fly ashes are extended, the extended setting time is ascribed to the secondary influences of dilution of the portland cement content.
- — The one high-calcium fly ash examined by Dodson (25.5% CaO) had a strong influence on setting time, causing a reduction. This may be ascribed to the inherent hydraulic characteristics of this particular ash, a property exhibited by many subbituminous ashes.

The observation of reduced setting time in the presence of high-lime fly ashes is by no means general. Ramakrishnan et al. (43) studied the setting time of mortars from concretes made with Type I and Type III cements with and without fly ash (20.1% CaO). The data from their study are shown in Figure 3.1. It is clear that in the presence of high-lime fly ash, setting was retarded for both types of cements with the effect being minimal for Type III cement.

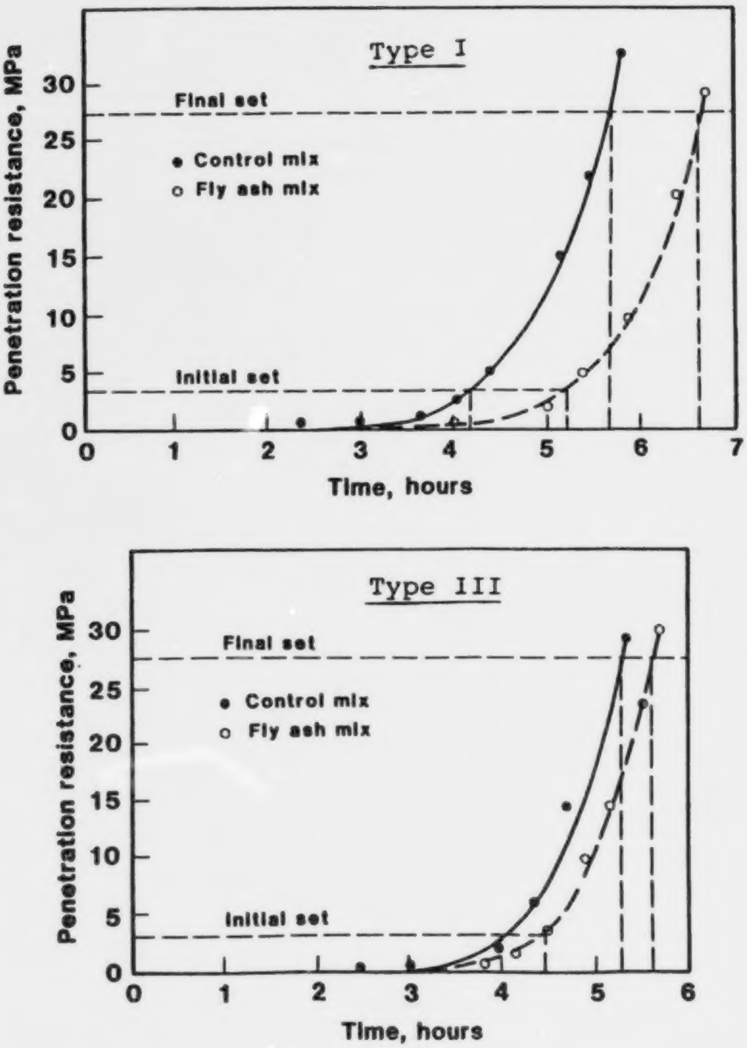

Fig. 3.1 — Comparison of setting time of control and fly ash concretes (43)

Effect of Fly Ash on Workability, Water-Requirement, and Bleeding of Fresh Concrete

The small size and the essentially spherical form of low-calcium fly ash particles have been credited with influencing the rheological properties of cement pastes; this causes a reduction in the amount of water required for a given degree of workability from that required for an equivalent paste without fly ash. In this respect, as noted by Davis et al. (2), fly ash differs from other pozzolans that usually increase the water requirement of concrete mixes. Advantage can be taken of the improved workability to reduce the amount of water used in a concrete and yet to maintain the same workability as non-fly ash concrete.

According to Owens (44), the major factor influencing the effects of ash on the workability of concrete is the proportion of coarse material (>45 μm) in the ash. He has shown that, for example, substitution of 50% by mass of the cement with fine particulate fly ash can reduce the water demand by 25%; a similar substitution using ash with 50% of the material greater than 45 μm has no effect on water demand. The general effect of coarse fly ash particles on the water demand is illustrated in Figure 3.2.

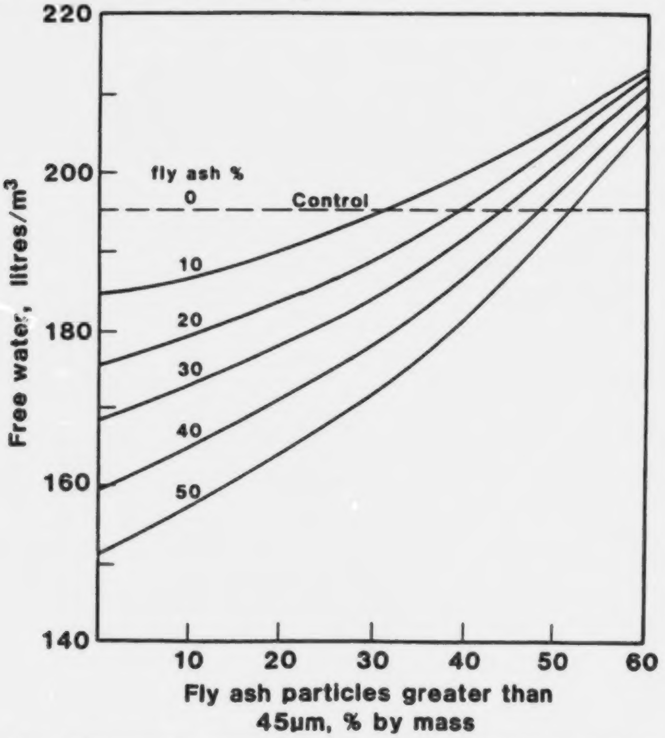

Fig. 3.2 — Influence of coarse particulate content of fly ash on the water required for equal workability in concrete (44)

Pasko and Larson (45) examined the amount of water required to maintain a nominal 63-mm slump in concrete mixes with partial replacement of cement by fly ash. They found that the water requirement was reduced by 7.2% in a mix in which 30% fly ash replaced 20% cement.

During investigations of the concrete materials for construction of the South Saskatchewan River Dam, Price (22) found that water requirement was not increased when additions of fly ash were made to concrete proportioned with fixed cement contents. The resulting concrete had a lower ratio of water to total cementitious material, yet workability and cohesiveness of the mixes were improved.

Compton and MacInnis (46) reported that a concrete made by substituting 30% of the cement with an eastern Canadian fly ash required 7% less water than was required for a control concrete of equal slump.

Brown (47) examined the workability of four concretes of different water-to-cement ratios in which ash was substituted for cement on an equal volume basis. Slump, time of flow, as measured in Vebe consistometer test, and compacting factor were measured for each mix. It was found that both slump and workability increased with increased ash substitution. The changes were found to depend upon the level of ash substitution (small additions sometimes being ineffectual) and on the water content. An empirical estimate was made which indicates that for each 10% of ash substituted for cement, the compacting factor changed to the same degree as it would by increasing the water content of the mix by 3 to 4%.

In another series of experiments, Brown determined the effects of ash substitution for equal volumes of aggregate or sand in one concrete, keeping all other mix proportions (and the aggregate grading) constant. The test concrete was modified by replacing either 10, 20, or 40% of the volume of sand by ash, or 10, 20, or 40% of the volume of the total aggregate by ash. The replacement of 40% of the total aggregate gave a mix that was unworkable.

It was concluded from Brown's work that when ash was substituted for sand or total aggregate, workability increased to reach a maximum value at about 8% ash by volume of aggregate. Further substitution caused rapid decreases in workability.

Brink and Halstead (48) reported that some fly ashes reduced the water requirement of test mortars, others (generally of higher carbon content) showed increased water requirement above that of control mortars. Welsh and Burton (49) reported loss of slump and flow for concretes made with some Australian fly ashes used to partially replace cement, when water content was maintained constant. Rehsi (50) reported that experience with a number of Indian fly ashes showed that all those examined increased the water requirement of concrete. In general, poor water demand characteristics have been found for fly ashes from older power plants where high carbon and coarse particle sizes are prevalent.

Recent work at CANMET (38) has also shown that water reduction does not always accompany the inclusion of fly ash, even with ash of otherwise acceptable properties obtained from modern power plants. Of the 11 fly ash concretes for which data are presented in Table 3.2, nine showed significant increases in slump at constant water content.

Because of the importance of workability to the proportioning of fly ash concretes, considerable effort has been made in recent years to develop a theoretical understanding of the rheology of fresh fly ash concrete.

In simple terms, the cement, water, fly ash, and fine sand particles, forming the paste in a mix, fill the void spaces between aggregate particles and, by coating them, provide cohesion and plasticity to the fluid mass.

Tattersall (51) has described the rheological behaviour of fresh concrete (at the low shear rates that are important in practice) in terms of a Bingham model* such that:

$$\tau - \tau_o = \mu_p \times \gamma$$

where:

τ = shear stress
γ = shear rate
τ_o = yield value
μ_p = coefficient of plastic viscosity.

Tattersall, and subsequently other co-workers, developed apparatus, described in detail by Tattersall and Banfill (52), to investigate the rheology of concrete based upon the Bingham model*. Ellis (53) has reported similar studies on concretes proportioned for mass and volume replacement of cement by fly ash.

Hobbs (54) has developed mathematical expressions relating the yield value and the plastic viscosity to volumetric parameters of concrete, and has shown these to be in agreement with viscosity data obtained by Ivanhov and Zacharieva (55) on fly ash–cement pastes and with workability measurements made by Brown (56) on concretes in which fly ash partially replaced cement.

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*The Bingham Model of flow describes the relationship between shear stress (τ) and shear rate (γ) for a fluid which is non-Newtonian to the extent that, for shear to occur, a certain level of shear stress must be applied (called the yield stress). Once the yield stress is exceeded, further shear stress induces Newtonian behaviour, and shear strain becomes proportional to shear stress.

For concrete in which the aggregate is replaced by fly ash, Hobbs' theory predicts that the yield value and the plastic viscosity decrease as the volume of fly ash increases, until minima are reached, and then increase as the aggregate replacement level is further increased. Hobbs concluded that the observed changes in slump, as the percentage of aggregate replaced by fly ash is increased, are in broad agreement with the changes in yield value and plastic viscosity for a Bingham suspension.

Ivanhov and Zacharieva (57), using vibro-viscometers, found similar effects produced by fly ash in concrete. They too established that fresh concrete can be approximated by the Bingham model and reported as follows:

- Yield stress and plastic viscosity were both found to be inversely related to the water-to-cement ratio, the extent of this relationship depending upon the surface area of the fly ash.
- Fine ash was found to be more effective at improving workability than was coarse ash.
- Plastic viscosity was found to increase with an increase in the volume of paste at a constant ratio of ash to total cementitious material.

In essence then, these preliminary efforts to determine yield stress and plastic viscosity and to develop a theoretical base for understanding concrete rheology, indicate that fly ash can act to *plasticize* concrete.

Concrete using fly ash is generally reported to show reduced segregation and bleeding and to be more satisfactory than plain concrete when placed by pumping. An example of data relating to bleeding of fresh concrete is given in Figure 3.3 (58).

Copeland (59) reported that in the field the use of fly ash was found to reduce bleeding in concretes made from aggregates known to produce harsh mixes normally prone to bleeding. Johnson (60) reported that most concrete made in the Cape Town (South Africa) area suffers from excessive bleeding due to a lack of fines in the locally available dune sands. He added that the problem can be overcome by increasing the overall paste volume by using fly ash in the concrete.

In the CANMET study (38), it was found (see Table 3.2) that six of the 11 ashes examined had increased bleeding when compared to that of control concrete.

In line with the improved rheological properties, and as a result of the fine particulate content, some fly ashes give a very marked improvement in finish when used as a replacement for either sand or cement. Effects such as these make fly ash particularly valuable in lean mixes and in concretes made with aggregates deficient in fines.

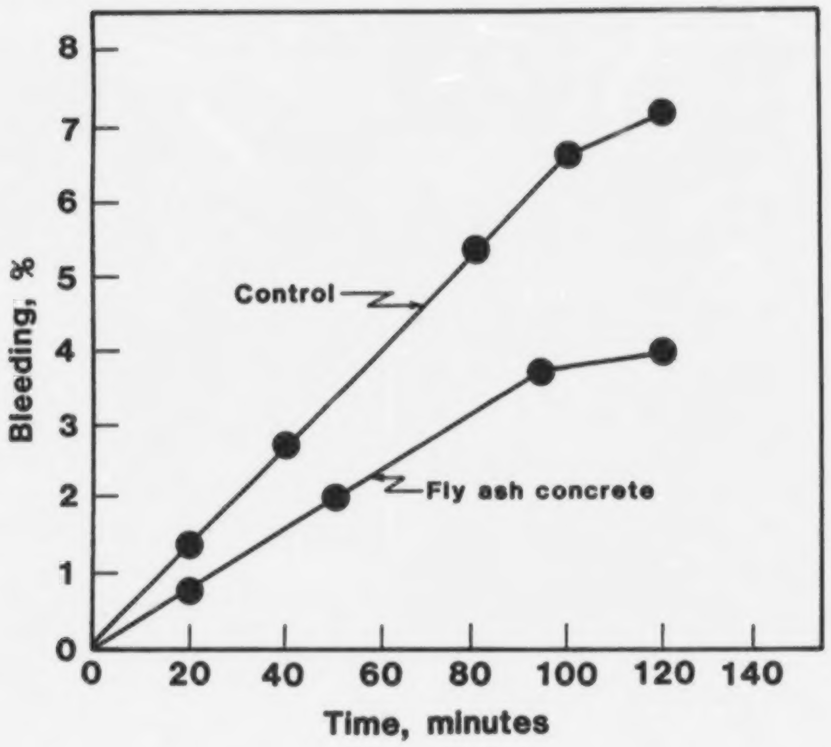

Fig. 3.3 — Relative bleeding of control and fly ash concretes (58)

Effect of Fly Ash on Temperature Rise of Fresh Concrete

The hydration or setting of portland cement paste is accompanied by an evolution of heat that causes a temperature rise in concrete. Replacement of cement by fly ash results in a reduction in the temperature rise in fresh concrete. This is of particular importance in mass concrete where cooling, following a large temperature rise, can lead to cracking. The first major use of fly ash in concrete was in the construction of a gravity dam where it was employed principally to control temperature rise (61).

Data reported by Elfert (62) show the beneficial effects of fly ash and a calcined diatomaceous shale on reducing the temperature rise of mass concrete.

Compton and MacInnis (46) reported the temperature–time curves shown in Figure 3.4 for two experimental concretes, one of which was made with a 30% substitution of an eastern Canadian fly ash for cement.

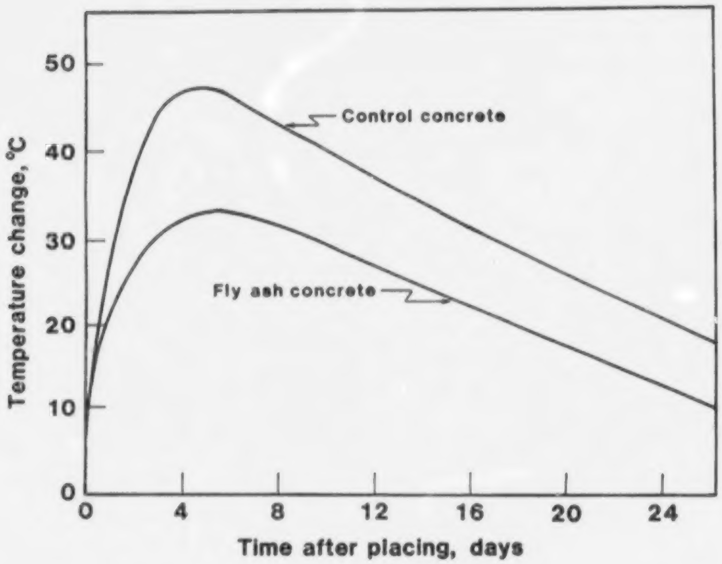

Fig. 3.4 — Temperature rise curves for fly ash and plain concrete test sections (46)

In modern construction, the use of mass concrete is no longer confined to structures such as dams. It is frequently used in foundations and structural members for many classes of buildings. The American Concrete Institute, Committee 116 (63), has defined mass concrete as:

> "... any volume of concrete with dimensions large enough to require that measures be taken to cope with generation of heat of hydration from the cement and attendant volume change to minimize cracking."

It has been estimated that the contribution of fly ash to early-age heat generation ranges from 15 to 30% of that of an equivalent mass of portland cement (36).

Temperature rise, of course, depends upon more factors than the rate of heat generation, including the rate of heat loss and the thermal properties of the concrete and its surroundings. Williams and Owens (64) have presented an estimation (Fig. 3.5) of the effect of element size on the temperature rise in fly ash concretes.

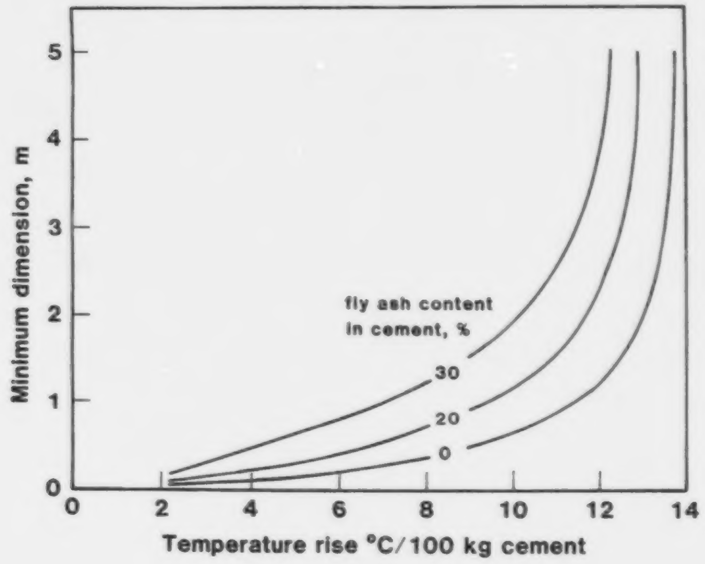

Fig. 3.5 — Effect of unit minimum size on the temperature rise in fly ash and plain concrete (64)

Bamforth (65) has reported on an extensive study of mass concrete containing fly ash or granulated blast-furnace slag as a substitute for cement. Included in this research was an in-situ investigation of the temperature rise and the resulting strain in three large foundation units.

Three concretes were examined:

- — a control mix with a portland cement content of 400 kg/m^3;
- — a mix with 75% of the portland cement replaced by granulated slag;

- — a mix with 30% of the portland cement replaced by a bituminous fly ash.

The concretes were placed in three foundation units each 4.5 m deep, the volumes ranging from 144 to 212 m^3. The units were instrumented to measure temperature changes and movement during the early stages of the heat-generation cycle. The measured temperature variation in each unit at mid-height is shown in Figure 3.6. As may be anticipated, the larger the quantity of cement replaced by fly ash or slag, the slower is the rate of temperature rise and the lower is the maximum temperature reached at any point in the concrete mass.

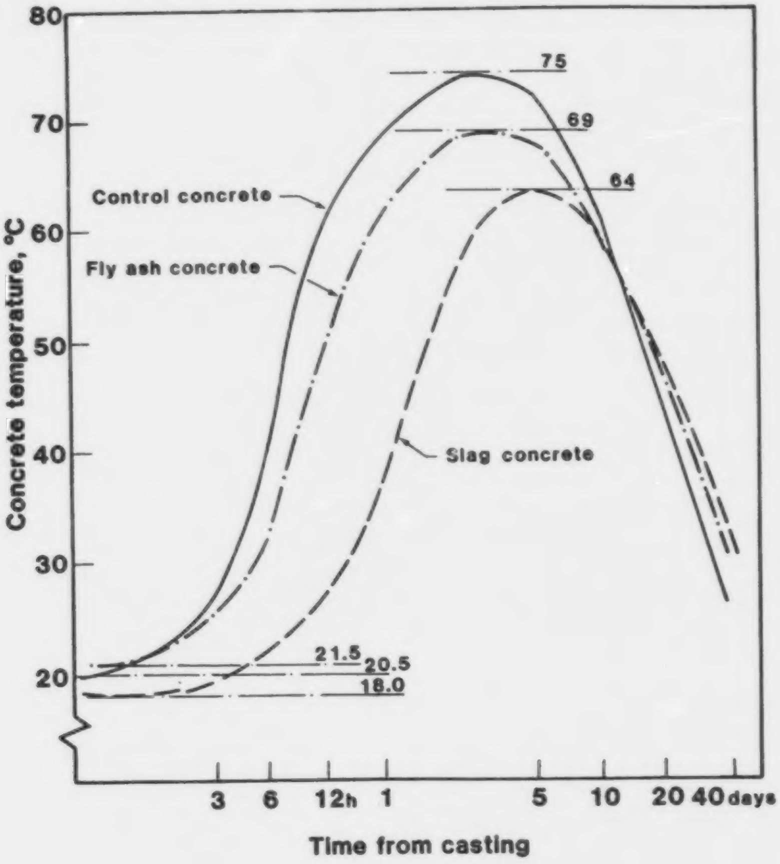

Fig. 3.6 — Variation of temperature recorded at mid-height in fly ash, slag, and plain concrete foundation units (65)

Although it is probably reasonable to assume that all low-calcium fly ashes will reduce the rate of temperature rise when used as cement replacement, high-calcium fly ashes do not necessarily cause reduced heat evolution. In general, the rate of heat evolution parallels the rate of strength development (66). Some high-calcium ashes react very rapidly with water, thus generating excessive heat.

Crow and Dunstan (66) have reported adiabatic temperature rise data on concrete mixes, where concrete containing 25% of a low-calcium fly ash showed a reduced rate of heat generation, and concrete with 25% of a high-calcium fly ash produced as much heat (at a similar rate) as a portland cement control.

Korac and Ukraincik (67) have reported data from in-situ measurements of temperature rise for concrete containing high-calcium (22.93% CaO) fly ash from brown coal. Concrete made with cement containing 50% fly ash showed less temperature rise than a concrete with commercially available cement containing 5% pozzolan and 15% slag.

Effects of Fly Ash on Air-Entrainment in Fresh Concrete

Cycles of freezing and thawing are extremely destructive to water-saturated concretes that are not properly proportioned. Concrete will be frost-resistant if it is properly air-entrained, is properly protected until some maturity has developed, and is made with sound coarse aggregate.

To obtain the desired number of correctly spaced air voids in hardened concrete that are necessary for frost resistance, an air-entraining admixture (AEA) is added in a prescribed dosage to the concrete during mixing. Two attributes are important: the AEA must produce the required volume of air bubbles of the desired size and spacing in the concrete; it must do so in a manner that allows the air content to remain as a stable dispersion while the concrete is mixed, transported, and placed.

It has been reported that the use of some fly ashes causes an increase in the quantity of air-entraining agent required to produce a given level of air-entrainment in fresh concrete (45,68–70).

Larson (69), presenting work on the use of fly ash in air-entrained concrete and reviewing the work of other investigators (70–74), concluded that the primary effect of fly ash was upon AEA demand, rather than upon air-entrainment as such.

In a study of six Type IP cements, Perenchio and Klieger (75) found that AEA requirements were higher in every case for the Type IP cements than for comparable Type I cements. Increases ranged from 15 to 210%. AEA demand in fly ash concrete was generally ascribed to the adsorption of air-entraining agents by carbon in the fly ash. A similarly wide range of AEA demand was found in the CANMET study (see Table 3.2) with most of the fly ashes examined.

The problem of air-entrainment of fly ash concretes has been the most frequently quoted factor impeding their widespread acceptance in construction in Canada. Recent research has fostered some better understanding of this problem.

Consideration of air-entrainment requires examination of three properties:

- — air content
- — stability of air content
- — air-void parameters in the hardened concrete.

Air content and the stability of air content are discussed in this section in relation to fresh concrete. The parameters of air-void systems and other issues related to the freezing and thawing resistance of hardened concrete are considered in Section 7.

Gebler and Klieger (76) have examined ten different fly ashes representing a range of chemical and physical properties. Concretes were proportioned by simple replacement of 25% of the cement by fly ash (by mass). All mixes were proportioned to have 75±25 mm slump and 6±1% air. The only air-entraining admixture used was neutralized Vinsol resin.

The AEA demand of the control concrete (for 6% air content) showed the following results:

- — For ashes containing more than 10% CaO, the range of AEA demand was 126 to 173%.
- — For ashes containing less than 10% CaO, the range of AEA demand was 170 to 553%.

Gebler and Klieger offered the following summary of the findings and conclusions relevant to air-entrainment in fresh concrete:

> "Generally, concretes containing Class C fly ash require less air-entraining admixture than those concretes with Class F fly ash. All concretes with fly ash required more air-entraining admixture than the portland-cement concretes without fly ash.
>
> "Plastic concrete containing Class C fly ash tended to lose less air than concretes with Class F ash.
>
> "As the air-entraining admixture requirement increases for a concrete containing fly ash, the air loss increases.
>
> "Air contents in plastic concrete containing Class F fly ash were reduced as much as 59%, 90 minutes after completion of mixing.

> "As the organic matter content, carbon content and loss-on-ignition of fly ash increase, the air-entraining admixture requirement increases as does the loss of air in plastic concrete.
>
> "Generally, as total alkalis in fly ash increase, the air-entraining admixture requirement decreases.
>
> "As the specific gravity of a fly ash increases, the retention of air in concrete increases. Concrete containing a fly ash that has a high lime content (Class C fly ash) and less organic matter tends to be less vulnerable to loss of air.
>
> "Generally, as the SO_3 content of fly ash increases, the retained air in concrete increases."

Fly ash is not alone in causing increased AEA demand in fresh concrete. Other mineral by-products behave in a similar manner, and some portland cements have been found to require excessive additions of air-entraining admixtures (77–81).

Burns et al. (82) have reported that pre-exposure of fly ash containing carbon to chlorine gas, calcium hypochlorite, or some surfactants effectively reduced the demand for air-entraining admixture in concrete. This was interpreted as being evidence of the active nature of the carbon in fly ash and its deactivation by the adsorption of chemically reactive species that did not themselves interfere with air-entrainment.

To date, no adequate theory has been developed to explain the various observations related to the interference that is sometimes observed between fly ash and air-entraining agents. Clearly, research is needed into the mechanisms of air-entrainment of concrete and into the ways that supplementary cementing materials influence the behaviour of air-entraining admixtures.

4. EFFECTS OF FLY ASH ON THE STRUCTURAL PROPERTIES OF HARDENED CONCRETE

Fly ash affects most of the properties of hardened concrete in one way or another. This section is concerned with the ways in which the use of fly ash influences the following properties:

- strength development
- elasticity
- creep, shrinkage, and thermal expansion.

A recent CANMET study (38) has shown that concretes made under similar conditions, from the same cement and aggregates, but incorporating different fly ashes, may develop strength at markedly different rates. Table 4.1 shows the strength development up to 91 days of the concrete mixes presented in Table 3.1 (see Section 3); the different reactivities of the fly ashes are clearly seen from these data.

Strength Development in Fly Ash Concrete

As discussed in Section 2, the main factors determining strength in concrete are the amount of cement used and the water-to-cement ratio. In practice, these are established as a compromise between the needs of workability in the freshly mixed state, strength and durability in the hardened state, and cost. The degree and manner in which fly ash affects workability is a major factor in its influence on strength development. As was shown in Section 3, a fly ash that permits the total water requirement to be reduced in concrete will generally present no problems with regard to the selection of mix proportions permitting any desired rate of strength development.

This section is concerned with the factors, other than mix-proportioning and workability, that determine the rate of strength development in fly ash concrete. In essence, these are the fundamental characteristics of fly ash that mix-proportioning seeks to accommodate in practice.

Many variables influence the strength development of fly ash concrete, the most important being the following:

- the properties of the fly ash
- chemical composition
- particle size
- reactivity
- the temperature and other curing conditions.

Table 4.1 — Properties of hardened concrete*

Mixture no.**	Compressive strength of 150 × 300-mm cylinders, MPa				Flexural strength of 75 × 100 × 400-mm prisms, MPa		
	7 days	28 days	91 days	365 days	14 days	28 days	91 days
Control	23.4	30.6	34.9	39.2	4.9	5.4	5.9
F1	18.4	25.7	31.4	38.3	4.4	4.4	5.4
F2	16.9	25.2	34.8	37.0	3.9	4.8	5.5
F3	14.4	21.0	27.6	34.4	4.0	5.0	5.3
F4	17.8	23.3	32.3	36.9	4.1	4.4	5.2
F5	20.1	28.0	33.9	44.3	3.5	4.4	5.3
F6	18.4	24.8	31.8	39.2	3.5	4.6	5.6
F7	16.7	24.1	29.1	35.7	3.9	4.5	5.4
F8	17.9	27.7	29.0	40.4	4.6	5.0	6.1
F9	16.7	24.9	31.1	35.6	4.3	4.2	5.7
F10	19.2	28.5	33.7	39.7	4.1	5.1	5.8
F11	21.1	29.4	35.3	40.1	4.8	5.3	6.6

*From reference 38.

**See Tables 3.1 and 3.2 for fly ash and mix proportion data.

Effect of fly ash type on concrete strength

The first difference between fly ashes that should be recognized is that some are cementitious even in the absence of portland cement. Frequently, these are the so-called Class C or high-calcium fly ashes usually produced at power plants burning subbituminous or lignitic coals.

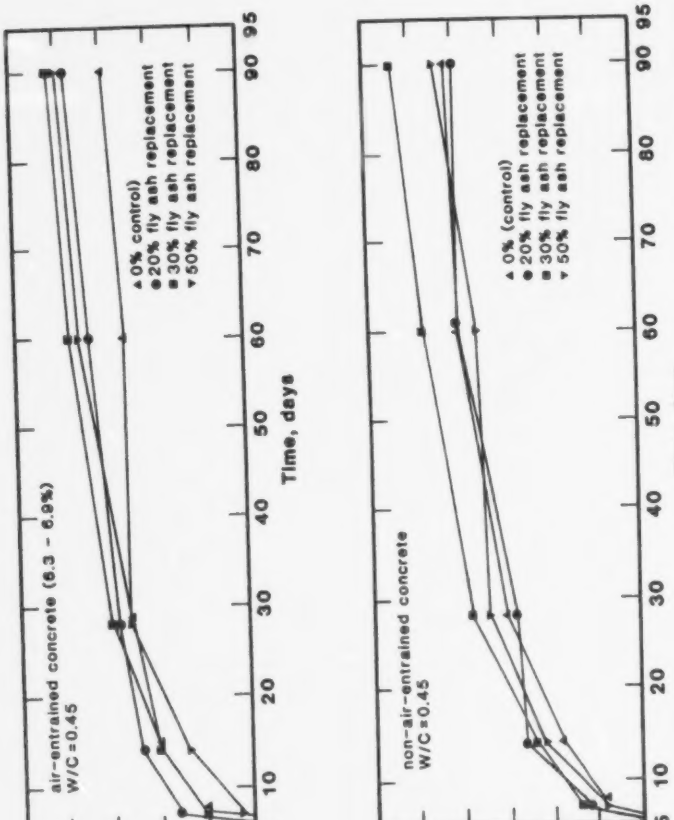

Fig. 4.1 — Compressive strength development of concretes containing high-calcium fly ash (83)

In general, the rate of strength development in concretes tends to be only marginally affected by high-calcium fly ashes. A number of authors have noted that concrete incorporating high-calcium fly ashes can be made on an equal weight or equal volume replacement basis without any significant effect on strength at early ages (83,84).

Yuan and Cook (83) have examined the strength development of concretes with and without high-calcium fly ash (CaO = 30.3%). The data from their research are shown in Figure 4.1. Using a simple replacement method of mix-proportioning they found the rate of strength development of fly ash concrete to be comparable to that of the control concrete, with or without air-entrainment.

Raba and Smith (84) examined the concrete-making properties of a sub-bituminous fly ash (CaO = 20.0%). Data on compressive strength gain attributed to the presence of high-calcium fly ash are shown in Table 4.2. It should be noted that the mix-proportioning approach used comprised replacement of fine aggregate by volume, the mass of cement and coarse aggregate being kept constant for each series of determinations.

Table 4.2 — Compressive strength gains attributed to the presence of high-calcium fly ash*

		Compressive strength**		
Cement	Fly ash	Per cent of control		Per cent gained
kg/m³		28 days	56 days	From 28 to 56 days
91	50	318	354	15.2
	59	352	393	16.0
	68	401	435	13.6
	77	471	494	10.5
136	50	210	228	10.2
	59	231	256	11.8
	68	245	269	11.1
	77	253	274	10.3
182	50	149	155	8.2
	59	153	167	12.4
	68	163	177	12.0
	77	187	190	6.2

*From reference 84.

**Note: In these mixes, fly ash was used to replace fine aggregate.

Low-calcium fly ashes, the so-called Class F ashes, usually formed from bituminous coals, were the first to be examined for use in concrete, and much that has been written on the behaviour of fly ash concrete has been determined by examination of materials using Class F ashes. In addition, the ashes used in much of the early work came from older power plants and were coarse in particle size, contained unburned fuel, and were often relatively inactive as pozzolans. Used in concrete, proportioned by simple replacement, these ashes showed exceptionally slow rates of strength development. Such observations have led to the development of generalized opinions that "fly ash reduces strength at all ages" (85). Conversely, they have resulted in considerable efforts to understand the factors affecting strength in fly ash concrete and the ways in which to manipulate them to obtain desired rates of strength gain.

Particle size and strength of fly ash concretes

Particle size can influence strength development in two ways. First, as discussed in Section 3, particles larger than 45 μm appear to influence water requirement in an adverse way. Thus, they act counter to the needs of the proportioning methods used to compensate for the slow rate of reaction of fly ash at early ages. Second, cementing activity occurs on the surface of solid phases, through heterogeneous processes involving the diffusion and dissolution of materials in concentrated pastes. Surface area must play a considerable role in determining the kinetics of such processes.

Direct experimental evidence of the influence of particle size on strength development is contradictory.

In a study of 36 concrete mixes, most containing fly ashes of a wide variety of properties, Crow and Dunstan (66) concluded that:

> "...fineness of ash compared loosely with the pozzolanic activity, thus finer ashes reacted more readily with portland cement. Fineness appeared more critical to the reaction of the low-calcium ashes than to those higher in calcium content."

Wesche and vom Berg (86), on the other hand, found no correlation between fineness and compressive strength of mortars at 7 or 28 days and a minor correlation at 90 days from more than 340 tests on fly ashes from 14 sources.

In some respects, these results are to be expected when samples from a large number of sources are examined in experiments designed to determine only one factor. Many fly ash-related variables influence strength development; poor correlation with particle size only indicates that particle size is not *the dominant variable* in fly ash reactivity. To establish a relationship to particle size, it is necessary either to limit all other variables to a minimum number or to perform a multi-variable experiment. To date, only the former approach has been taken.

Both Joshi (87) and Ravina (88) have exploited the phenomenon of particle size segregation that occurs in electrostatic precipitators, to obtain fly ash fractions of different fineness from a single source.

When fly ash is collected in a multi-stage, electrostatic precipitator, segregation by particle size occurs; particles in the finer size categories are collected in the chambers furthest from the furnace. By taking ash from each chamber, particles of different size distributions from the same source are obtained at the same time.

Unfortunately, size is not the only factor that differs between the chambers. The chemical properties, density, and morphology of the particles also differ. Chemically, carbon tends to be segregated with the larger particles, and alkali sulphates and chlorides tend to be collected on the surface of the finer particles in the cooler regions of the precipitator. Low-density particles are differentially distributed in the precipitator; cenospheres and irregularly shaped particles tend to precipitate from the gases in the first chamber and, thus, affect average density measurements. However, examination of ashes from one source, segregated by size, would seem to be the simplest way of determining the influence of particle size on strength, given the limitation that the results may be weighted by other, uncontrolled factors.

An alternative way to obtain sized ash from one source is by grinding. Monk (89) has examined ashes from four base-load power plants as blended cements and as interground cements with portland cement. The principal conclusions from his research were:

- Portland-fly ash cements prepared by intergrinding clinker, gypsum, and fly ash have a water demand equal to, or lower than, that of equivalent cements produced by blending ordinary portland cement and fly ash.
- Intergrinding did not negate the workability benefit of fly ash. Breakdown of spherical particles was not observed, but the agglomerates of spheres in coarse ashes were separated.
- Compressive strengths at all ages for the interground cements were equal to, or higher than, those for the blended cements.
- Intergrinding resulted in an improvement of coarse ashes, with respect to water-reducing properties, and also pozzolanic activity, as indicated by compressive strength improvement at later ages.

Fly ash reactivity

Pozzolanic activity, although well established as a phenomenon, is far from being well understood. Much of the research currently in progress on fly ash is directed to the understanding of pozzolanic reactions. It is not within the scope of this chapter to discuss this work in any detail, and the reader is referred to other published sources (19,90–93) for review material on this subject.

However, some aspects of pozzolanic reactivity are of immediate relevance to the behaviour of fly ash concrete in the hardened state. In particular, the effects of temperature during curing on the subsequent strength of concrete are of great practical importance and, as will be discussed, appear to be closely related to the fundamental nature of pozzolanic action.

Temperature and the development of strength in fly ash concretes

When concrete made with portland cement is cured at temperatures in excess of 30°C, an increase is seen in strength at early ages but a marked decrease in strength is noted in the mature concrete (94).

Concrete containing fly ash behaves significantly differently. Figure 4.2 shows the general way in which the temperature, reached during early ages of curing,

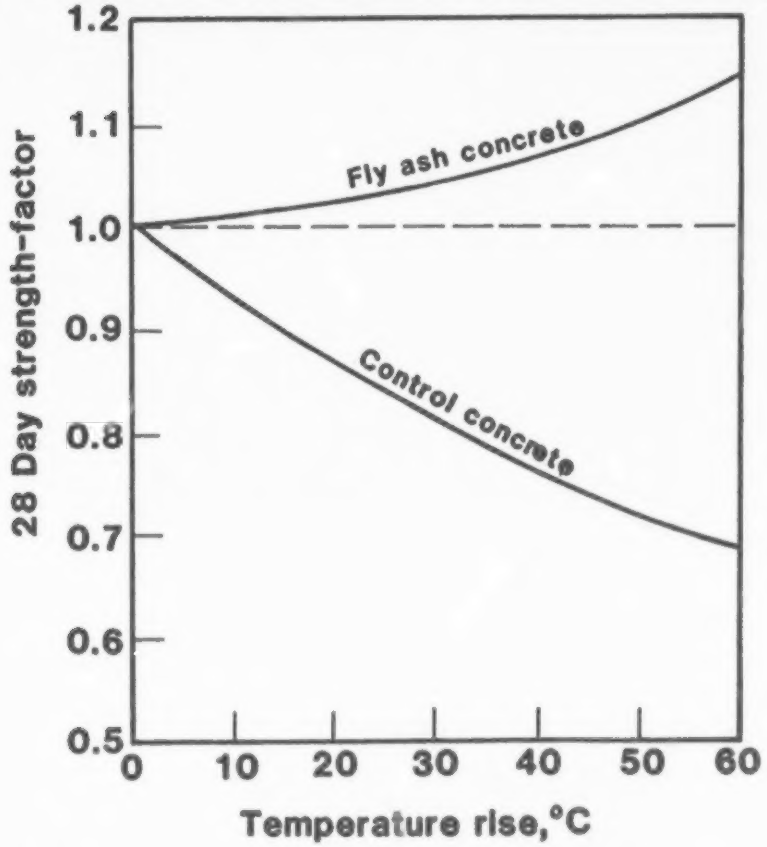

Fig. 4.2 — Effect of temperature rise during curing on the compressive strength development of concretes (64)

influences the 28-day strength of concrete. In contrast to the loss of strength that occurs with ordinary portland cement, fly ash concretes show strength gains as a consequence of heating. This is of great value in the construction of mass concrete or in concrete construction at elevated temperatures.

Kobayashi (95) reported that fly ash was used at a 25% cement replacement level in the concrete for an intake tunnel of the Kurobegwa No. 3 Power Station in Japan (96). Because this tunnel is located in rock at temperatures of 100 to 160°C, fly ash was used as a means to combat the loss of strength that would have resulted had portland cement concrete been used alone.

Ravina (97) has discussed how the effects of fly ash in concrete cured at moderately elevated temperatures can be used to advantage in precast operations. Ravina's paper is of considerable interest also with regard to the way in which fly ash was found to react in concrete cured under a controlled regime that included some exposure to heat.

Ravina examined concrete made with fly ash from the same source but of two size fractions:

— coarse ash from the first precipitator field with 30 to 35% retained on a 45-μm sieve;

— fine ash from the third precipitator field with 14 to 17% retained on a 45-μm sieve.

The following curing regimes were used:

— Control specimens were kept for 22 hours at 23°C prior to demolding, and then placed for seven days in the fog-room at 23°C. They were then stored at 23°C and 65% RH until being tested.

— Thermally cured specimens were kept at 23°C for two hours and then transferred to a steam chamber where the temperature was raised from 23 to 75°C over a two-hour period and kept at 75°C for four hours. Heating was then discontinued and the specimens were allowed to cool in the chamber. After 22 hours the samples were demolded and then stored in the same conditions as the control specimens.

From the compressive strength data obtained in this study, the author drew the following conclusions:

— Large quantities of fly ash may be used effectively in concrete cured at elevated temperatures, with a significant improvement in its compressive strength, in contrast to the rather limited contribution under normal curing conditions at ages up to 28 days.

- The beneficial effect of curing at elevated temperatures, on coarse and fine fly ash concrete, is significant at an early age and continues to later ages.

Ravina's work and the observations of other authors (4,64) raise some significant issues with regard to the nature of pozzolanic reactivity. The following would seem to warrant further investigation:

- The rate of reaction of fly ash–cement systems is clearly increased by temperature, as is the case for portland cement. Yet the products of hydration do not exhibit the poor mechanical properties associated with curing portland cement at elevated temperatures. This would suggest that the products of fly ash–cement hydration, their relative proportions or their morphology, are significantly different from those formed from thermally accelerated hydration of portland cement alone.
- The rate of reaction of fly ash in cement systems is so significantly increased by temperature, that the effects of particle size on pozzolanic behaviour are largely overcome. This suggests that some pozzolanic activity tests that use thermal acceleration may give seriously misleading results.
- The pozzolanic reaction, once initiated by heat, appears to continue when the source of external heating is removed, even with coarse fly ash. This indicates the possible existence of an activation effect, similar to that observed for slags, that has not previously been associated with pozzolanic activity.

The sensitivity of fly ash to elevated temperature implies that it will also be sensitive to reduced temperature with a consequent reduction in the rate of strength development. This has been observed in practice and it is generally noted that fly ash concretes require more attention to curing in cold weather.

Effect of Fly Ash on Elastic Properties of Concrete

Published data indicate that fly ash has little influence on the elastic properties of concrete.

Abdun-Nur (16) makes the following observations on the early literature citations.

> "The modulus of elasticity of fly ash concrete is lower at early ages, and higher at later ages (2,98). In general, fly ash increases the modulus of elasticity of concrete when concretes of the same strength with and without fly ash are compared (99–101)."

Lane and Best (40) state as follows:

> "Fly ash properties controlling the compressive strength of concrete also influence the modulus of elasticity but to a lower extent. The modulus of elasticity, like compressive strength, is lower at early strength and higher at ultimate strength when compared with concrete without fly ash."

Crow and Dunstan (66), reporting on an examination of the properties of 36 concretes, most containing fly ash at different levels and from different sources, concluded as follows with regard to elastic properties:

> "The elastic properties of concretes containing both portland cement and fly ash are similar to those expected with portland cement (alone). The modulus of elasticity and Poisson's ratio both increased with age, paralleling the compressive strength development. The modulus of elasticity ranged from a low at 28 days of 18.8 GPa to a high of 39.6 GPa at 365 days. Most of the ashes (in concrete) had a 28 day Poisson's ratio in the range of 0.14 to 0.25."

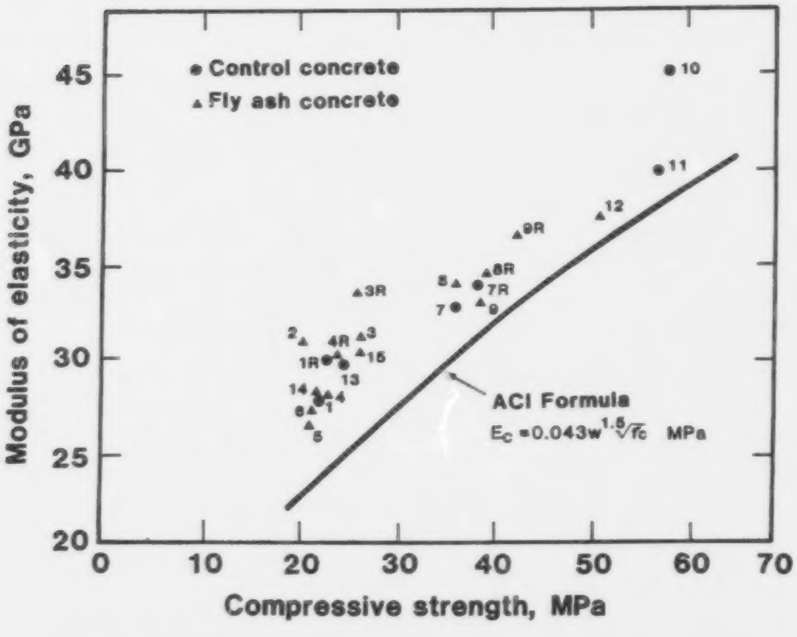

Fig. 4.3 — Moduli of elasticity of fly ash concretes (102)

Ghosh and Timusk (102), studied fly ash concretes, proportioned for equivalent 28-day strength, over a range of nominal strength values. They showed the relationship between strength and modulus of elasticity reproduced in Figure 4.3 and concluded that for all strength levels the modulus of elasticity of fly ash concrete is generally equivalent to that of the reference concrete. In all instances, the modulus was found to exceed that given by the ACI formula.

Nasser and Marzouk (103) examined the effects of temperature on modulus of elasticity of concrete made from fly ash (from a Saskatchewan lignite source) and a sulphate resistant, ASTM Type V cement. They reported that over the range of temperature 21 to 232°C, the modulus of elasticity was reduced by up to 40% for specimens that were both sealed and unsealed to prevent moisture loss.

Effect of Fly Ash on Creep Properties of Concrete

Data on creep of fly ash concrete are limited. Lohtia et al. (104) have reported the results of studies of creep and creep recovery under stress–strength ratios of 20 and 35% of plain and fly ash concretes made by replacing cement with equal weights of fly ash in the range of 0 to 25%. From this work they drew the following conclusions:

- Replacement of 15% of cement by fly ash was found to be the optimum value with respect to strength, elasticity, shrinkage, and creep for the fly ash concrete studied.
- Creep–time curves for plain and fly ash concretes were similar with creep linearly related to the logarithm of time.
- Increase in creep with fly ash content up to 15% was negligible. However, slightly higher creep took place at fly ash contents higher than 15%.
- The creep coefficients were similar for materials with fly ash contents in the range of 0 to 25%.
- Creep recovery was found to vary from 22 to 43% of the corresponding 150-day creep. For cement replacement beyond 15%, the creep recovery was smaller. No definite trend of creep recovery as a function of stress–strength ratio was observed.

Among more recent studies, Ghosh and Timusk (102) have examined bituminous fly ashes of different carbon contents and fineness values in concretes at nominal strength levels of 20, 35, and 55 MPa (water-to-cement ratios 1.0, 0.4, and 0.2, respectively). Each concrete was proportioned for equivalent strength at 28 days. In the majority of specimens, it was found that fly ash concretes showed less creep than the reference concretes. This was attributed to a relatively higher rate of strength gain after the time of loading than for the reference concretes.

Yuan and Cook (83) reported the data in Figure 4.4 from studies of high-strength concrete containing a high-calcium fly ash, which showed fly ash concrete containing 30 and 50% ash to exhibit more creep than either the control concrete or a concrete with 20% ash. More extensive data from this study are discussed in Section 6 of this chapter in regard to the use of fly ash in high-strength concrete.

Gifford and Ward (105), examined lean mass concrete and concluded that fly ash reduces creep as a result of a number of factors including the following:

- Fly ash increases the elastic modulus.
- It contributes to the total aggregate and reduces the volume of paste available to creep.

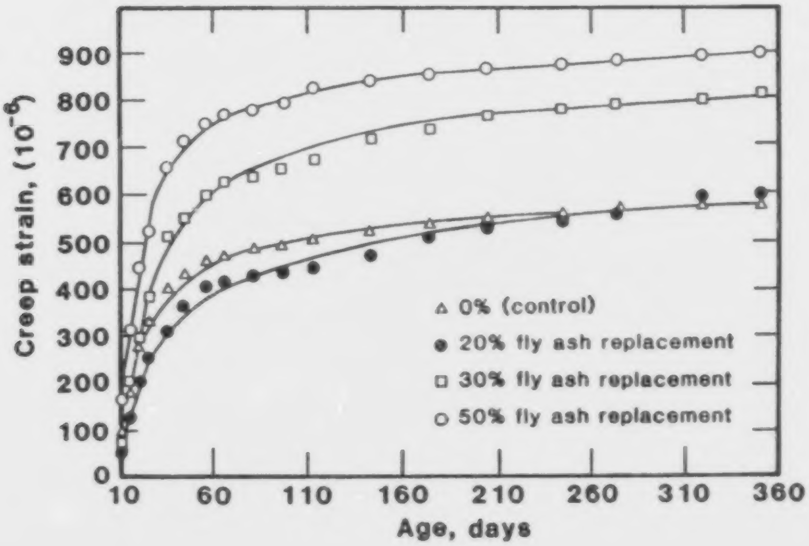

Fig. 4.4 — Creep of fly ash concretes (83)

Effect of Fly Ash on Load-Independent Volume Changes of Concrete

It has been generally reported that the use of fly ash in normal proportions does not significantly influence the drying shrinkage of concrete. Typical of the conclusions of most researchers in this respect are those made by Davis et al. (2) who comment as follows:

> "For masses of ordinary thickness, such as are normally found in highway slabs and in the walls and frames of buildings, the drying shrinkage at the exposed surfaces of concrete up to the age of one year is for fly ash cements about the same as, or somewhat less than, that for corresponding portland cements. At a short distance from the exposed surface the drying shrinkage up to the age of one year is substantially less for concretes containing corresponding portland cements.
>
> "For very thin sections and for cements of normal fineness the drying shrinkage of concretes containing finely ground high-early-strength cements may be somewhat reduced by the use of fly ash."

Studies reported by Elfert (62), comparing the drying shrinkage and autogenous length change of fly ash concrete with plain concrete and concrete made with other pozzolans, show that fly ash concrete performed better in these respects than the other concretes studied.

In a more recent study, Ghosh and Timusk (102) showed that for the same maximum size of aggregate and for all strength levels, the shrinkage of concrete containing fly ash is lower than that for non-fly ash concrete.

In their studies of concrete using high-calcium fly ash, Yuan and Cook (106,83) concluded that the replacement of cement by fly ash has little influence on drying shrinkage. Their data are shown in Figure 4.5. Similar conclusions may also be drawn from the data on shrinkage obtained by CANMET (38) for concretes incorporating a range of fly ashes (Table 4.3).

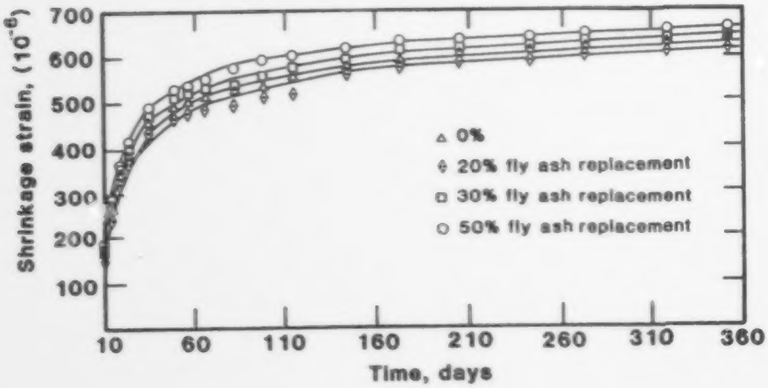

Fig. 4.5 — Drying shrinkage of concretes incorporating high-calcium fly ash (83)

Table 4.3 — Drying shrinkage of fly ash concretes*

Mixture no.**	Duration of drying, days	Shrinkage measurements			
		Initially cured for 7 days in water		Initially cured for 91 days in water	
		Moisture*** loss, %	Drying shrinkage, x10^{-6}	Moisture*** loss, %	Drying shrinkage, x10^{-6}
Control 2	224	55.0	422	53.7	453
F1	224	57.5	447	47.9	365
F2	224	57.3	364	45.4	280
F3	224	56.9	411	56.2	405
F4	224	54.7	379	49.2	387
F5	224	58.8	404	51.1	403
F6	224	60.6	475	56.4	454
F7	224	64.3	397	54.1	433
F8	224	56.3	400	—	327
F9	224	58.2	390	49.3	361
F10	224	58.4	642	55.2	500
F11	224	49.5	454	48.9	362

*From reference 38.

**See Tables 3.1 and 3.2 for fly ash and mix proportion data.

***As a percentage of total original water.

Munday et al. (107) have reported typical shrinkage–age relationships for fly ash concretes as shown in Figure 4.6 and have concluded that a general relationship exists between drying shrinkage and equivalent cement content (Figure 4.7). It was also found that wetting and drying of fly ash concrete resulted in a cumulative expansion over a number of cycles. It was concluded that overall, the incorporation of fly ash does not significantly affect the drying shrinkage, wetting/drying expansion, or thermal expansion of concrete.

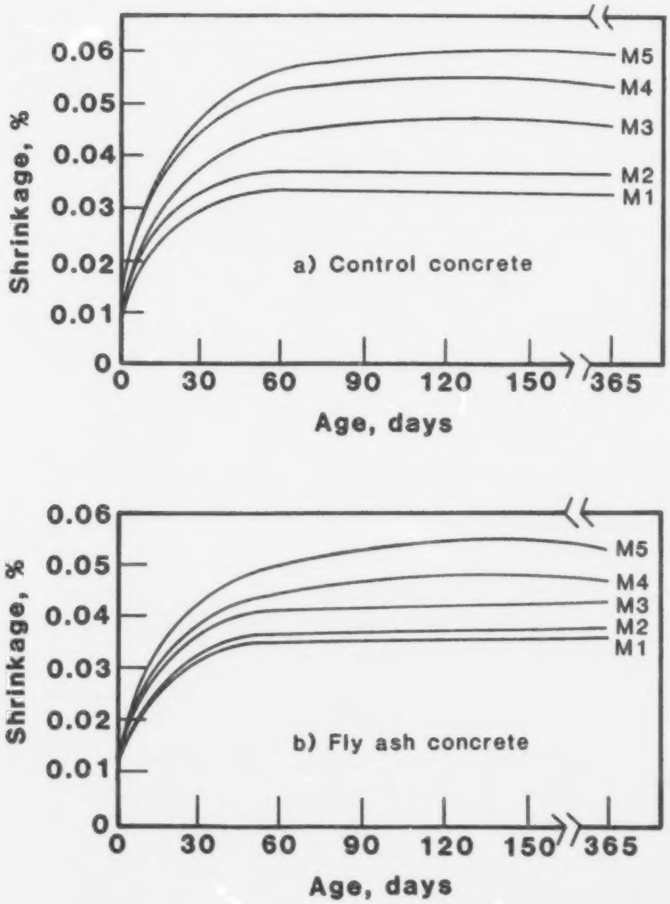

Fig. 4.6 — Drying shrinkage of concretes incorporating low-calcium fly ash (107)

Thermal expansion of concrete is mainly affected by the thermal expansion of the coarse aggregate that constitutes its main component. Values for wet limestone and quartzite have been reported to be 4.0 and 11.7 micro-strain per °C, respectively, and cement paste is reported to vary from 11.0 to 20.0 micro-strain per °C (105). Gifford and Ward (105) quote Dunstan as suggesting that fly ash slightly reduces thermal expansion; their own data indicated an average reduction of 4% at a fly ash level of 40%.

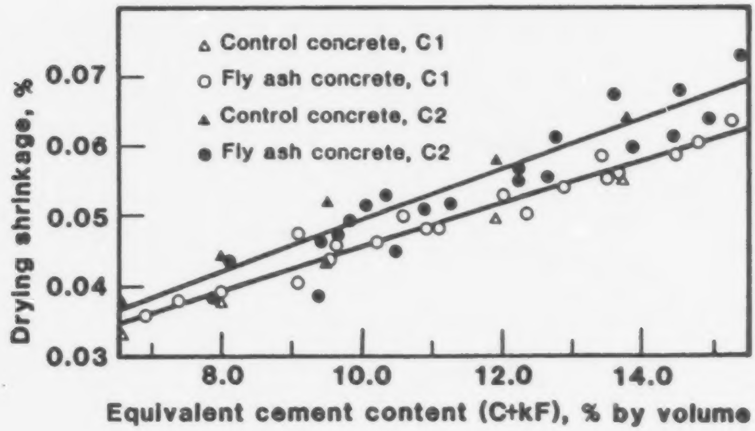

Fig. 4.7 — Drying shrinkage of concretes versus equivalent cement content (107)

5. USE OF FLY ASH IN CONCRETES FOR SPECIALIZED APPLICATIONS

For most construction applications, the decision whether to use fly ash in concretes will be made largely on the basis of the availability of materials, local concrete practice and, most important, economics. There are, however, some types of special concretes that require the use of fly ash or other mineral by-products to attain specified properties. In particular, high-strength concretes (>50 MPa at 28 days) and roller-compacted mass concretes both depend on the use of fly ash for their structural and economic success.

High-Strength Concretes

High-strength concretes can be classified broadly into three groups:

- concretes in the strength range from 35 to 70 MPa used over the past ten years in a number of construction applications;
- concretes ranging in strength from 70 to 100 MPa;
- concretes with compressive strength in excess of 100 MPa.

As Wolsiefer has noted (108), although field-placeable concrete in the strength range from 70 to 120 MPa is now commercially available, the major documented uses of high-strength concrete in building applications have been for 62 MPa concrete in the Chicago area. Thus, for now, consideration of the use of fly ash in high-strength concrete must be restricted to the lower end of the above strength range.

High-strength concrete is used for a number of reasons, the most important being:

- to minimize the size of concrete structural members in buildings;
- to obtain more rapid production cycles in the pre-cast and prestressed concrete industry;
- to obtain high strength and modulus of elasticity in structural members built to withstand large stresses.

In general, the production of high-strength concrete requires the use of low water-to-cement mixes with sufficient workability to permit placement in a heavily reinforced structure. To meet these requirements, the following factors are usually considered important (109,110):

- use of high cement contents (up to 550 kg/m^3) at slumps of 75 to 100 mm;

- — stringent selection of cement and aggregates;
- — use of low water-to-cement ratios, attained through the employment of water-reducing agents and superplasticizers (see Section 6);
- — use of pozzolans, especially fly ash.

Fly ash functions in high-strength concrete to provide at least two benefits:

- — A good-quality fly ash generally will permit the water content of a concrete mix to be reduced without loss of workability (see Section 2).
- — Fly ash produces increased strength at late ages of curing that cannot be achieved through the use of additional portland cement.

Typical mix proportions for high-strength concrete used in two structures built in the Chicago area during the 1970's are given in Table 5.1; the resulting compressive strength values obtained with these mixes are given in Table 5.2. Concrete mixes incorporating fly ash and using similar proportions, with strengths of 55 MPa, have been used in construction in the Toronto area (111).

Table 5.1 — Mix proportions and properties of fresh high-strength concretes*

	Quantity, m3	
Material	Water Tower Place	River Plaza
Cement (kg)	383.7	385.6
Fine aggregate (kg)	464.9	471.7
Stone (kg)	816.5	784.7
Water (kg)	136.1	149.7
Water-reducing admixture (mL)	751.1	1271.5
Fly ash (kg)	45.4	45.4
Slump (mm)	114.3	114.3
Air content (%)		1.5
Unit weight (kg/m3)	2433.4	2383.8

*From reference 109.

Table 5.2 — Compressive strengths of high-strength concretes*

Age, days	Compressive strength, MPa					
	Water Tower Place			River Plaza		
	Air**	Moist	Cores	Yard	Jobsite	Cores
7		52.68			50.40	46.54
28	63.09	64.81		71.29	64.88	55.85
56	0	72.95		77.50	72.40	73.71
90	64.95			80.19	78.67	72.12
180	63.50			91.15		
365	66.88					
730	61.78		79.71			

*From reference 109.

**7 days' moist-curing followed by curing at 50% RH, 21°C.

Table 5.3 — Mix proportions and properties of fresh and hardened high-strength concretes of constant ash/cement ratio*

	Nominal cement content, kg/m³				
	279	335	390	446	502
Materials (kg/m³)					
Cement	282	341	396	449	501
Fly ash	71	85	99	112	131
Limestone	1144	1147	1141	1130	1121
Sand	735	643	578	513	454
Water	148	157	161	169	179
W/R admixture (mL/m³)	696	851	967	1083	1238
Properties of fresh concrete					
Slump (mm)	102	102	114	102	95
Unit weight (kg/m³)	2379	2373	2376	2373	2374
W/(C+F)	0.42	0.37	0.33	0.30	0.28
F/C	0.25	0.25	0.25	0.25	0.26
Compressive strength (MPa)					
7 days	44.3	48.1	53.1	55.1	59.3
28 days	54.6	62.7	67.4	72.7	70.2
56 days	61.0	68.0	75.7	75.9	78.0
90 days	63.3	68.9	75.0	75.7	75.0
180 days	67.8	76.9	83.6	86.6	85.3

*From reference 112.

Cook (112) has reported on a comprehensive investigation of concretes in the strength range from 50 to 75 MPa (28 days) made using a high-calcium fly ash (CaO = 30.3%). Table 5.3 illustrates how fly ash can contribute to the strength development of high-strength concretes and the flexibility in selection of mix proportions that can be used to obtain essentially similar concretes. In Table 5.3, the concrete properties attained by using different quantities of cementitious materials at a constant ash-to-cement ratio (0.25) are presented. As the cement factor was increased, sand content and the water-to-cementitious material ratio was reduced. Strength at 28 days could be controlled over a range of 55 to 70 MPa.

Roller-Compacted Concrete

In the 1970's, a method for the construction of dams termed *roller compaction* was proposed (113–116). The method, which in many ways is more related to the procedures used in geotechnical engineering than to conventional concrete practice, depends upon the placement of layers of a low-workability concrete in the interior of a dam and its compaction using vibratory rollers.

The American Concrete Institute (117) describes roller-compacted concrete (RCC) as a dry concrete material that is consolidated by external vibration using vibratory rollers. It differs from conventional concrete in its required consistency, in that for effective consolidation RCC must be dry enough to support the weight of the placement equipment, but fluid enough to permit distribution of the paste throughout the mass during mixing and compaction.

Roller-compacted concrete must satisfy four requirements:

— It must have a high density with a minimum of air voids.

— The layers of concrete must bond together (116).

— The generation of heat in the dam must be minimized.

— The hardened concrete must have a high capacity to withstand tensile strains to resist thermal cracking.

Three types of materials have been investigated and used for RCC:

— cement-stabilized, soil-like materials;

— lean concrete, with a cementitious content of 100 to 150 kg/m^3, of which up to 30% may be fly ash;

— rich concrete, with a cementitious content of 180 to 270 kg/m^3 of which 60 to 80% may be fly ash.

Roller-compacted concretes can be made from any of the basic types of portland cement in combination with pozzolans. In regard to proportioning, the principal difference between the selection of the relative quantities of the cementitious components in RCC as compared to more conventional concretes relates to the use of large quantities of fly ash.

The principal function of fly ash in RCC is to occupy space between larger particles by providing a large volume of fine material that would otherwise require the use of additional cement.

Roller-compacted concrete is normally required to have a high paste content. Dunstan (118) has shown that as the paste-to-mortar ratio falls below 0.35 to 0.38, the density of the compacted mass is significantly reduced. Below this level of paste content, all the voids in the fine aggregate are not being filled. To obtain maximum density, the paste content must be increased; however, to attain this by the addition of portland cement results in two serious disadvantages:

— The rate of heat evolution increases and the possibility of thermal cracking becomes greater.

— The cost of the concrete may become uneconomical.

The desired approach to obtain maximum density RCC is to use large volumes of fly ash to increase the paste content.

Pozzolanic activity is somewhat secondary, in that strength in RCC can develop over long periods after placement. As the ACI Committee report states (117):

> "Where there is a deficiency in finish (in RCC) a pozzolan does not have to be highly reactive to be effective. Thus, many fly ashes whose reactivity, due to insufficient particle fineness, would not meet... ASTM specifications would be suitable for most roller compaction applications."

Typical RCC mix proportions and corresponding strength data, as reported by ACI Committee 207, are shown in Tables 5.4 and 5.5.

As in more conventional mass concrete, fly ash contributes to reducing the rate of heat evolution and, hence, the extent of temperature rise.

Permeability of roller-compacted concrete used in the Upper Stillwater Dam was reported to be equal to, or less than, conventional mass concrete (119).

Both air-entraining and water-reducing admixtures have been used at normal dosages in roller-compacted concrete. ACI committee 207 (117) states that these admixtures are effective in reducing the vibration time for full consolidation. However, the effectiveness of air-entraining admixtures in roller-compacted concrete and the appropriate dosage rates are as yet not established.

Table 5.4 — Mix proportions for some roller-compacted concretes*

		Mix data				
		Weights, kg/m³				
Source	Maximum aggregate size, cm	Cement	Pozzolan	Water	Fine aggregate	Coarse aggregate
1	7.6	56	77	77	60	1649
2	11.4	139	0	80	618	1774
3	7.6	139	0	86	683	1691
4	7.6	139	0	83	676	1602
5	7.6	42	78	83	676	1602
6	3.8	75	164	89	745	1426
7	3.8	45	178	84	727	1438
8	3.8	116	139	103	657	1438

*From reference 117.

Table 5.5 — Properties of some roller-compacted concretes*

			Shear strength, MPa	
Source	Age, days	Compressive strength, MPa	Mass	Joint
1	138	23	4	2
2	72	26	5	1
3	66	23	6	
4	120	23	6	3
5	120	16	4	1
6	90	26		3
7	90	18	2	2
8	90	41		

*From reference 117.
Note: For mix proportions, see Table 5.4.

The use of roller-compacted concrete is not restricted to mass structures such as dams. It has been employed to replace rip-rap for erosion control of a floodway sill in Alaska, as a foundation rock protection, in a lock floor, and in other structures (120).

As Joshi (121) has pointed out, roller-compacted concretes are closely related to the family of *stabilized materials* commonly used for pavements and other applications. The use of roller-compacted and lean concrete containing high amounts of fly ash has been extensively studied for pavement construction in Britain. Sherwood and Potter (122) have reported studies of *ash-modified lean concrete* for use in road-bases. They suggest that ash-modified lean concrete should be equal in performance to conventional lean concrete provided that the development of thermal and shrinkage cracks was similar and that it could withstand repeated traffic-induced stress at early ages.

6. FLY ASH CONCRETE INCORPORATING CHEMICAL ADMIXTURES AND MINERAL BY- PRODUCTS

In recent years, the use of chemical admixtures and mineral by-products, such as slags and condensed silica fume, has become relatively common. If fly ash is used in concrete, its interaction with, or influence upon, the efficiency of other *admixtures* must be considered. This section examines interaction of fly ash with other materials used to modify concrete properties.

Chemical Admixtures

In concrete technology, the term *chemical admixtures* is used to describe soluble substances excluding air-entraining admixtures that are used as ingredients of a concrete mix to modify its properties. Most chemical admixtures react with cement. They may be classified into four groups:

- ***Retarders*** include many organic and inorganic compounds, frequently derived from industrial by-products related to lignosulphonates.
- ***Accelerators*** are mostly inorganic salts of calcium or alkali metals, the most common being calcium chloride.
- ***Water reducers*** include a very broad range of surface-active agents, with or without set-retarding capacity, based upon lignosulphonates and hydroxy-carboxylic acids. Their main function is to disperse and deflocculate cement particles.
- ***Superplasticizers**** fall into one of the following classes:
    - sulphonated melamine-formaldehyde condensates
    - sulphonated naphthalene-formaldehyde condensates
    - modified lignosulphonates
    - other surfactants.

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*Also termed high-range water reducers.

In general, the concern with regard to possible fly ash/admixture interactions results from the experiences that have been commonly reported on the interference of fly ash and other finely divided particulates with the efficiency of air-entraining agent activity in fresh concrete (see Section 3). Because of the generally accepted view that air-entraining agents are adsorbed on fine particulates other than cement, it is not unreasonable to anticipate that similar problems may arise with other admixtures that rely on surface activity for their effect.

In the case of superplasticizers, this issue has been studied directly (123,124). Uchikawa et al. (123) have reported that, for three types of superplasticizers examined, adsorption on fly ash was less than on cement in water suspensions. This was attributed to differences in the surface properties. The fly ash used was of a low-calcium type and, hence, the results should not be considered to be generally applicable to all fly ash types.

Nagataki et al. (124) examined the adsorption of a naphthalene-type superplasticizer on several fly ashes of different carbon contents. The authors reported that the adsorption of superplasticizer appears to be reduced in the presence of carbon, in clear contradiction to the reported behaviour of air-entraining agents (see Section 3).

Contrary observations were reported by Uchikawa et al. (125) for two classes of anionic surfactant superplasticizers and five low-calcium fly ashes in direct comparison with air-entraining agents. The results from this study indicate some degree of inter-dependence between the carbon content of a fly ash and its capacity to adsorb superplasticizers.

It is clear from the generally contradictory nature of the reported data that much research remains to be done on the interaction of surfactants with fly ash and the consequent effects on the efficiency of chemical admixtures in fly ash concrete.

Accelerators

Mailvaganam, Bhagrath, and Shaw (41) have reported studies of the effects of chloride and non-chloride accelerators and a superplasticizing admixture on fly ash concretes cured at two different temperatures. Their data, shown in Table 6.1 indicate that both chloride and non-chloride accelerators are effective in the presence of fly ash. They do not, however, completely compensate for the slow rate of early strength development that results from the use of simple substitution of ash for cement on an equal quantity basis.

Table 6.1 — Properties of fly ash concretes incorporating chemical admixtures*

Mix	Admixture**	Compressive strength, MPa				Shrinkage, % × 10^{-3}	
		3 days	7 days	28 days	90 days	28 days	56 days
1	—	23.3	28.5	35.4	41.1	86	100
2	—	13.1	16.8	24.6	36.1	92	103
3	CL	29.7	35.3	40.5	46.9	89	106
4	CL	16.6	20.9	30.9	40.1	94	106
5	MFS	32.6	36.9	43.0	47.2	102	112
6	MFS	18.0	21.6	30.2	41.4	99	120
7	NCL	26.3	31.0	37.5	42.7	82	98
8	NCL	14.6	18.5	26.7	38.3	87	95

*From reference 41.
**CL = Chloride accelerator (1.5% active solids).
MFS = Superplasticizer (0.6% active solids).
NCL = Non-chloride accelerator (0.68% active solids).
All at a dosage of 3% by weight of cementitious material.

Water-reducing admixtures

In 1962, the U.S. Corps of Engineers (126) reported work in which fly ash and water-reducing admixtures were combined in making special concrete structures. It was concluded from compressive and flexural strength determinations and estimated costs that such structures could be made more economically with these materials than with portland cement alone.

In 1971, Lovewell and Hyland (127) concluded from research and literature surveys that:

> "...combinations of pozzolans (including fly ash) with water-reducing agents, or with water-reducing-retarder agents, with and without air-entrainment can be used in concrete without creating abnormalities. All such ingredients should be checked for compliance with applicable standards and trial mixes should be made to check compliance of such mixes with specified quality parameters."

In 1975, Samarin and Ryan (128) reported studies made on fly ash concretes proportioned by the replacement–addition method and containing water-reducing admixtures. Two series of concrete trial mixes were reported: Series A in which a comparison was made between plain, fly ash, admixture, and fly ash plus admixture concretes of comparable consistency and compressive strength: Series B in which a comparison was made between plain and fly ash plus admixture concretes of three different strength levels. The comparative data from this research are given in Tables 6.2 and 6.3.

Table 6.2 — Compressive strengths of water-reduced concretes*

Mix type	Compressive strength, MPa			
	3 days	7 days	28 days	90 days
Series A				
Plain	25.4	30.1	40.6	41.6
Fly ash	23.8	31.1	44.5	49.8
Admixture	22.8	31.5	41.3	44.6
Fly ash admixture	20.5	28.5	39.8	49.5
Series B				
Plain	31.3	34.2	47.5	54.7
Fly ash admixture	28.7	35.4	47.5	56.4
Plain	26.0	30.5	41.5	46.5
Fly ash admixture	21.3	29.0	39.7	52.0
Plain	13.7	18.9	27.5	31.6
Fly ash admixture	13.3	19.0	30.4	42.7

*From reference 128.

Superplasticized concretes

During the past few years, there has been an increase in the use of superplasticizing admixtures for one of three purposes:

— to increase the fluidity of fresh concrete proportioned with *normal* water-to-cement ratios, and thus to produce what has been termed flowing concrete;

— to permit reduction in the cement content of concrete while maintaining the same water-to-cement ratios;

— to reduce greatly the quantity of water used while maintaining the same cement content and slump, thus achieving very low water-to-cement ratios.

To correctly proportion flowing concrete (concrete with slump in excess of 180 mm), it is desirable to use more sand than is employed in conventional concrete. However, it has been found that instead of incorporating excessive amounts of sand, it is preferable to use fly ash to provide the necessary fine particles that give cohesiveness to the mixes (129). It is to be expected that there will be an increased use of fly ash in the future for this application.

Table 6.3 — Properties of concretes incorporating cement, fly ash, and water-reducing admixtures[*]

Series	Mix type	Cementitious content, wt %		Water demand, kg/m³	Slump, mm	Air, %	Bleeding capacity, kg/m²	Setting time, h:min		Strength at 28 days		Modulus of elasticity, 10⁴ × MPa
		Portland	Total					Initial	Final	Compressive, MPa	Tensile, MPa	
A	P	15.2	15.2	188	80	3.1	2.5	4:45	6:45	40.6	3.95	3.65
	F	14.1	16.7	182	90	2.3	2.2	4:40	6:15	44.6	4.38	3.61
	A	13.7	13.7	165	80	5.7	2.1	6:20	8:30	41.3	4.00	3.52
	F-A	13.1	15.7	170	80	5.2	2.0	6:30	9:05	39.8	4.10	3.41
B	P	19.1	19.1	196	80	2.4	0.9	4:10	5:35	47.5	4.49	3.68
	P	15.2	15.2	185	85	2.8	2.4	4:40	6:15	41.5	4.52	3.50
	P	12.2	12.2	193	80	3.8	4.9	5:30	7:30	27.5	3.56	2.98
	F-A	17.0	19.1	173	80	5.2	1.4	6:10	7:55	47.5	4.70	3.55
	F-A	13.1	15.7	169	80	5.3	2.5	6:30	8:25	39.7	3.78	3.30
	F-A	9.8	13.1	167	80	5.8	4.3	6:55	8:50	30.4	3.37	3.18

[*] From reference 128.

From an extensive laboratory study of the combined use of fly ash with superplasticizers, Lane and Best (130) have drawn the following conclusions:

- "...superplasticizers are compatible with fly ash in concrete and produce no detrimental effects. The benefits claimed for these admixtures in plain concrete, however, were not as apparent in fly ash mixtures, particularly with respect to compressive strength gains and duration of increased plasticity. Water reductions for equal slump did not exceed 15 per cent, improving this characteristic only slightly over a standard water-reducing agent. The low water reductions can be attributed to the lower water requirement for fly ash concrete as compared to plain concrete for equal consistencies. Since there is less excess water initially available, the addition of water reducers is less effective.
- "...superplasticizers are equally effective in attaining a temporary increase in concrete consistency for both fly ash concrete and plain concrete. The highly plastic phase diminishes after 15 minutes and ceases after about 30 minutes with fly ash concrete."

Ericksen and Nepper-Christensen (131) examined the water-reducing effects of a sodium naphthalene sulphonate superplasticizer on concretes incorporating two low-calcium fly ashes. They reported higher levels of water reduction than those found by Lane and Best (130), which was attributed to the higher cement content and larger dosage of admixture used in their study.

Brooks et al. (132) compared the behaviour of four concrete mixes:

- plain
- plain with superplasticizer
- fly ash
- fly ash with superplasticizer.

The mix proportions used for this study, which were selected to produce a minimum strength at 28 days of 30 MPa with a slump of 40–60 mm, are shown in Table 6.4. Compressive strength development largely reflected the effects of water reduction (Table 6.5) for both plain and fly ash concretes.

Swamy et al. (133) reported the data shown in Table 6.6 for flowing concrete (slump 260 to 280 mm) containing fly ash and proportioned to give compressive strengths at one day comparable to plain concrete. The advantageous effects of moist-curing versus air-curing on the strength development of fly ash concretes is seen clearly from these data.

Table 6.4 — Mix proportions for superplasticized concretes*

Materials	Mix number** 1	2	3	4
Cement (kg/m³)	314	314	219	219
Fly ash (kg/m³)			117.5	117.5
Aggregate/cement ratio	5.98	5.98		
Aggregate/cement + fly ash			5.58	5.58
Per cent fines	33.3	33.3	31.1	31.1
Water/cement ratio	0.57	0.48		
Water/cement + fly ash			0.46	0.35
Admixture % by weight of cement		1.60		
Admixture % by weight of cement + fly ash				1.60

*From reference 132.

**Mix 1 = plain concrete.
Mix 2 = plain concrete with admixture.
Mix 3 = fly ash concrete.
Mix 4 = fly ash concrete with admixture.

Table 6.5 — Properties of superplasticized concretes*

Property	Units	Mix number 1	2	3	4
Compressive strength	MPa				
1 day		13.0	19.0	11.0	18.5
7 days		37.5	50.5	31.0	39.5
28 days		48.5	61.0	44.5	53.0
Indirect tensile strength	MPa				
1 day		1.15	1.75	0.85	1.15
7 days		2.90	2.70	2.35	2.20
28 days		3.35	3.65	3.05	2.75
Static modulus of elasticity	GPa	34.0	34.0	31.5	37.0
Secant modulus of elasticity	GPa	31.0	37.5	31.0	35.0
Volume changes (water stored)	10^{-6}				
Creep		199	221	283	107
Swelling		25	37	123	39
Volume changes (air stored)	10^{-6}				
Creep		424	419	305	227
Shrinkage		400	485	506	584

*From reference 132.

Table 6.6 — Properties of flowing concrete*

Curing regime	Slump, mm	Age, days	Compressive strength,** MPa	Flexural strength, MPa
Air	265	1	12.0	1.8
		3	26.4	2.7
		8	36.1	3.3
		28	45.2	3.5
		43	50.8	4.1
3 days water and air	280	1	10.4	1.7
		3	24.6	3.0
		8	34.4	3.4
		28	48.0	4.3
		43	55.0	4.4

*From reference 133.

**Mix proportions, kg/m^3.

Cement	287
Fly ash	123
Sand	758
Gravel	881
Water	191

Superplasticizer added at 2.5% by weight of cement + fly ash.

Mukherjee, Loughborough, and Malhotra (134) have examined the use of superplasticizers to aid the incorporation of large percentages of fly ash into high-strength concrete. Three types of superplasticizers were examined:

- — superplasticizer M, a sulphonated melamine–formaldehyde condensate;
- — superplasticizer N, a sulphonated naphthalene–formaldehyde condensate;
- — superplasticizer L, a modified naphthalene–formaldehyde condensate.

The setting time, slump, density, and air content were determined for fresh concrete and the strength, elasticity, shrinkage, and creep were examined for hardened concrete specimens. The properties reported are presented in Tables 6.7 and 6.8. The experimental data were reported in relation to a reference fly ash concrete, proportioned to contain 37% fly ash and to produce a compressive strength of 40 MPa at 28 days.

Table 6.7 — Mix proportions and properties of fresh, superplasticized (high strength) concrete*

		Mix proportions, kg/m³							Properties of fresh concrete		
Mix	Batch	Cement	Fly ash	Fine aggregate	Coarse aggregate	Water	W/(C + F)	P**	Slump, mm	Air,*** %	Initial set, h:min
1	1	377	223	420	1105	208	0.35		65	1.5	4:40
	2	378	224	420	1107	208	0.35		70	1.5	4:40
	3	377	223	420	1105	208	0.35		65	1.4	4:40
	4	377	223	419	1103	209	0.35		65	1.4	4:40
2	1	389	230	433	1139	171	0.28	M 1.97	75	1.5	4:25
	2	388	230	432	1137	171	0.28	1.97	70	1.7	4:25
	3	390	231	434	1141	172	0.28	1.97	65	1.6	4:25
	4	389	230	433	1139	171	0.28	1.97	65	1.6	4:25
3	1	390	231	434	1141	172	0.28	N 0.86	70	2.0	5:15
	2	391	231	435	1145	172	0.28	0.86	70	1.8	5:15
	3	389	230	433	1139	171	0.28	0.86	70	1.9	5:15
	4	390	231	434	1143	172	0.28	0.86	70	1.9	5:15
4	1	390	231	434	1143	172	0.28	L 2.70	75	1.6	7:40
	2	391	231	435	1145	172	0.28	2.70	75	1.4	7:40
	3	390	231	434	1143	172	0.28	2.70	75	1.5	7:40
	4	389	230	433	1139	171	0.28	2.70	75	1.6	7:40

*From reference 134.
**P = % superplasticizer by weight of cement + fly ash.
***Entrapped air only.

Table 6.8 — Properties of hardened, superplasticized (high-strength) concrete*

Mix	Batch	Compressive strength of concretes, MPa						Flexural strength 28 days, MPa	Modulus of elasticity 28 days, MPa × 10^4	Shrinkage after 448 days dry storage	
		7	28	56	91	183	365 days			Shrinkage, %	Moisture loss, %
1	1		41.0		51.8			6.3	3.17	−0.0441	1.83
	2	28.8	37.9	51.9	51.5				3.43		
	3	25.0		41.4				6.8		−0.0453	1.84
	4					53.4	57.3				
2	1		53.3		65.2			8.3	3.48	−0.0413	1.19
	2	36.1	52.5	61.8	65.6				3.46		
	3	36.1		57.7				8.0		−0.0399	1.13
	4					70.0	69.8				
3	1		52.5		66.9			8.0	3.48	−0.0467	1.07
	2	36.8	53.8	61.7	67.1				3.46		
	3	36.8		63.2				7.4		−0.0427	
	4					66.3	74.7				1.08
4	1		51.0		62.7			7.8			1.19
	2	35.4	51.0	59.5	62.5				3.45	−0.0455	
	3	34.1		59.0				8.1	3.45		1.26
	4					63.4	62.5			−0.0454	

*From reference 134.

The following factors were noted:

- Satisfactory high-strength concrete can be obtained using large quantities of fly ash (low-calcium) and various superplasticizers.
- The mechanical properties of the water-reduced, superplasticized fly ash concrete were superior to the reference concrete.
- The workability may impose a limitation on its use for cast-in-place construction, due to a *gluey* texture at slumps between 65 and 75 mm.
- Superplasticizers N and L both increased the setting time markedly. It is not possible from the data to determine whether fly ash also influenced set-time. However, the data from Mailvaganam et al. (41) showed increases of 25% when melamine–formaldehyde sulphonate superplasticizer was used with fly ash in comparison with its use in a plain concrete mix.

Malhotra (135) examined the use of a sulphonated naphthalene–formaldehyde condensate superplasticizer in semi-lightweight concrete containing fly ash. The high strengths obtained at one day in the fly ash mixes (Table 6.9) were attributed to the combined effects of fly ash and superplasticizer in permitting extreme water reduction while retaining a practical level of workability.

Table 6.9 — Properties of semi-lightweight concrete incorporating fly ash and superplasticizer*

	Mix proportions				Strength MPa	
Cement	Fly ash, kg/m^3	Water	W/(C+F)	Superplasticizer, % on wt of cement	1 day	28 days
422		137	0.33	0.49	27.1	43.5
431		124	0.29	0.90	34.1	47.0
445		110	0.25	1.50	35.0	49.6
393	60	113	0.25	1.20	36.0	47.6
420	30	112	0.25	1.40	38.2	48.5

*From reference 135.

Superplasticized concretes exhibit marked increases in slump; however, these increases are of short duration. Within 30 to 60 minutes after addition of superplasticizer the concrete reverts to its original consistency. This loss of slump presents some difficulties in the use of superplasticizers.

Ryan and Munn (136) have examined the effects of fly ash on slump loss. They investigated concrete mixes in which all or part of the cement was replaced by the same volume of fly ash. The data obtained indicated that the rate of slump loss was not greatly affected when the binder was a mixture of cement and fly ash, regardless of the relative proportions. However, when the concrete contains no portland cement, superplasticizer addition also reduced slump, but the rate of slump loss was greatly reduced. It was concluded that the superplasticizers examined are chemically affected by reaction with lime liberated during the hydration of portland cement in a way that leads to loss of plasticity in the mix.

In general, although there remain many unanswered questions, it is clear that the combined use of fly ash and superplasticizers or water reducers allows for a wider flexibility in the proportioning of concrete for fluidity, strength, or economy. The concretes so obtained should be of particular value for applications in situations where resistance to chemical and environmental attack is important.

Further research work is urgently required to establish both the nature of fly ash–surfactant interactions and their practical effects in concrete.

Mineral By-Products

In addition to fly ash, other mineral by-products have been used as supplementary cementing materials. Some, specifically, ground, granulated blast furnace slag, have been used for many years in commercial concrete. Others, in particular condensed silica fume, have only recently been introduced and are largely in the developmental stages of application.

Slags develop strength in the presence of portland cement more rapidly than do most fly ashes. Furthermore, it is possible to substitute them for larger quantities of portland cement (up to 75–80%) while producing dense, durable concrete. Condensed silica fume is a very reactive pozzolan that develops high strength at low levels of substitution. Its main disadvantage is that, unlike fly ash, it causes a very marked reduction in workability and, hence, increases water demand.

Not unexpectedly, slags and condensed silica fume have been investigated as materials to be included with fly ash in concrete as a means of overcoming its two principal weaknesses:

- the relatively low level of cement substitution that is practical in structural concretes using fly ash;
- the relatively slow rate of strength development of fly ash concretes.

The combined use of slag and fly ash is not new. Ternary cements based on portland cement, granulated slag, and fly ash have been the subject of investigation (73,137–145) in a number of countries around the world and have been used on a commercial basis in France (137) and in Australia (146).

Combinations of condensed silica fume and fly ash in concretes are of more interest in that, at relatively high levels of fly ash substitution (30%) and low levels of condensed silica fume addition, considerable rates of early strength development are possible (147, 148).

Carette and Malhotra (147) have reported an extensive investigation of concretes containing cements made from 70% portland cement and 30% low-calcium fly ash, with additions of condensed silica fume in the range from 5 to 20%. Superplasticizer was used to compensate for the loss of slump consequent upon the use of condensed silica fume; in this way water content was kept constant.

Figure 6.1 shows typical strength development data for such concretes. The main features noted from this work were as follows:

- — The quantity of superplasticizer required to maintain a constant slump increased as the quantity of condensed silica fume was increased.
- — At 20% condensed silica fume, the rate of slump loss was rapid and the fresh concrete tended to be *gluey*.

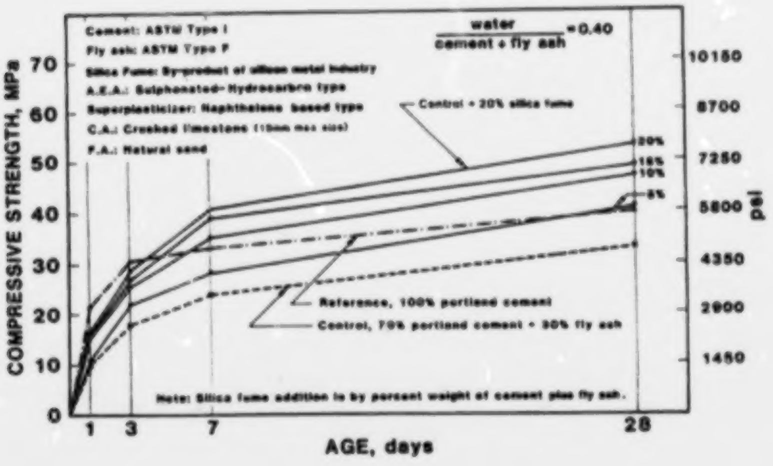

Fig. 6.1 — Compressive strength versus age for fly ash concretes with a W/(C+F) of 0.40, containing various additions of condensed silica fume (147)

- In general, regardless of the water-to-cementitious material ratio, strength at 1 and 3 days was higher for concretes incorporating condensed silica fume than for the control concrete (30% fly ash/70% portland cement) but lower than for an equivalent plain concrete.

- Pozzolanic action from the condensed silica fume was most apparent between 3 and 7 days; pozzolanic activity from fly ash became apparent after 28 days.

The most important aspect of the combined use of fly ash and condensed silica fume in the types of concrete studied is that at ages beyond seven days, the loss in compressive strength of concrete due to the incorporation of 30% of fly ash generally can be completely compensated by addition of as little as 10% condensed silica fume.

In view of the current interest in high-strength concretes and the desire, especially in the precast industry, for early strength development, it is to be expected that much more information will become available in the near future on the nature and performance of fly ash–condensed silica fume–portland cement concretes. Certainly, there is ample need for more research in this area where substantial cement saving (and hence energy savings) can be realized.

7. EFFECTS OF FLY ASH ON THE DURABILITY OF CONCRETE

Failure of concrete after a period of years less than the lifetime for which it was designed may be caused by the environment to which it has been exposed or by a variety of internal causes. External causes may be physical or chemical in nature: weathering, extremes of temperature, abrasion, or chemical action in the cement, aggregate, or reinforcement components. Internal causes may lie in the choice of materials or in inappropriate combinations of materials, and may be seen as alkali–aggregate expansion or other forms of failure. Of all the causes of lack of durability in concrete the most widespread is excessive permeability. Permeable concrete is vulnerable to attack by almost all classes of aggressive agents. To be durable, portland cement concrete must be relatively impervious.

Increasingly, concrete is being selected for use as a construction material in aggressive or potentially aggressive environments. Concrete structures have always been exposed to the action of sea water. In modern times, the demands placed on concrete in marine environments have increased greatly, as concrete structures are used in arctic, temperate, and tropical waters to contain and support the equipment, people, and products of oil and gas exploration and production. Concrete structures are used to contain nuclear reactors and must be capable of containing gases and vapours at elevated temperatures and pressures under emergency conditions. Concrete is increasingly being placed in contact with sulphate and acidic waters. In all of these instances, the use of fly ash as concrete material has a role, and an understanding of its effect on concrete durability is essential to its correct and economical application.

The following subsections provide a general view of the present knowledge regarding the durability of fly ash concrete. The subject matter is vast, complex, and as yet incompletely understood. The reader desiring a more detailed treatment of the subject is recommended to consult the cited research literature for more complete discussions.

Effects of Fly Ash on Permeability of Concrete

The movement into a concrete mass of aggressive solutions or the removal of the dissolved reaction products out of concrete must play a primary role in determining the rate of progress of concrete deterioration caused by chemical attack. Permeability of a concrete mass is therefore fundamental in determining the rates of mass-transport relevant to destructive chemical action. It should be recognized that all the cementitious hydrates and some of the aggregates from which concretes are made are inherently subject to attack, not only by sulphates, chlorides, acids, and organic agents, but by water alone. That concrete survives aqueous environments at all is attributable to (a) the low-equilibrium solubility of the hydrated components and (b) the low rate of mass transfer in well-compacted, cured concrete. Given any combination of cement and aggregate, it is generally observed that the less permeable the concrete, the greater will be its resistance to aggressive solutions or pure water.

A number of investigations have been made of the influence of fly ash on the relative permeability of concrete pipe containing fly ash substituted for cement in amounts of 30 and 50%. Davis (149) examined the permeability of concrete pipe incorporating fly ash substituted for cement in amounts of 30 to 50%. Permeability tests were made on 150 × 150-mm cylinders at ages of 28 days and 6 months (149). The results of these tests are shown in Table 7.1.

Table 7.1 — Relative permeability of concretes with and without fly ash*

Fly ash		W/(C+F)	Relative permeability	
Type	% by weight	by weight	28 days	6 months
None	—	0.75	100	26
Chicago	30	0.70	220	5
	60	0.65	1410	2
Cleveland	30	0.70	320	5
	60	0.69	1880	7

*From reference 149.

It is clear from these data that the permeability of the concrete was directly related to the quantity of hydrated cementitious material at any given time. After 28 days of curing, at which time little pozzolanic activity would have occurred, the fly ash concretes were more permeable than the control concretes. At 6 months, this was reversed. Considerable imperviousness had developed, presumably due to the pozzolanic influence of fly ash.

Kanitakis (150) used an *Initial Surface Absorption Test* to examine concrete with and without a low-calcium fly ash (CaO = 2.0%) made using the mix proportions shown in Table 7.2. Absorption measurements were made at 7, 17, 28, and 56 days of curing.

Table 7.2 — Mix designations and proportions for concretes examined by Kanitakis*

	Constituents, per m³				
Mix	Cement, kg	Fly ash, kg	Sand, kg	Stone, kg	Water, L
N	400		586	1190	233
M	350	100	519	1213	227

*From reference 150.

The author concluded that at early ages fly ash concrete behaves as a *lean-mix* concrete and is thus permeable. At later ages, permeability is reduced as the pozzolanic action proceeds.

The rather limited observations on this very important aspect of fly ash concrete are consistent with the view expressed by Manmohan and Mehta (151) that the transformation of large pores to fine pores, as a consequence of the pozzolanic reaction between portland cement paste and fly ash, substantially reduced permeability in cementitious systems.

Diffusion of ions, such as chlorides, that are not specifically bound by the components of concrete is reasonably represented by Fick's diffusion equation (152,153):

$$\frac{dc}{dt} = D_c \cdot \frac{d^2c}{dx^2}$$

where:

c = chloride ion concentration at a distance x, after a time t;

D_c = the chloride ion diffusion coefficient.

For concrete in offshore structures, Browne (152) has reported values for D_c of 1.0×10^{-9} to 50.0×10^{-9} cm²/s for high- and normal-strength concrete, respectively.

Short and Page (154) have reported on the diffusion of chloride ions in solution into portland and blended cement pastes and have found the following values of D_c for different cement types:

Type of cement	**$D_c \times 10^9$ (cm²/s)**
Normal portland	44.7
Sulphate-resisting	100.0
Fly ash/portland	14.7
Slag/portland	4.1

It was concluded from these data that slag and fly ash cements were more effective in limiting chloride diffusion in pastes than were normal or sulphate-resisting cements.

Permeability to gases, in particular to air and carbon dioxide, is important to some aspects of concrete durability related to carbonation (see below). Kasai et al. (155) examined the air permeability of mortars (moist-cured for 1, 3, and 7 days) of blended cements made with fly ash and with blast furnace slag and concluded:

- — The air permeability of blended cements is greater than that of portland cements.
- — When early moist-curing is extended, the permeability becomes reduced.

The considerable differences in the strengths at all ages of the mortars examined by these authors, with fly ash mortars being some 20 to 30% weaker, suggest that the curing regimes adopted were inadequate to permit any conclusions relevant to the practical behaviour of blended cement concretes in the field.

Effects of Fly Ash on Carbonation of Concrete

Calcium hydroxide and, to a lesser extent, the calcium silicates and aluminates in hydrated portland cement react in moist conditions with carbon dioxide from the atmosphere to form calcium carbonate. The process, termed carbonation, occurs in all portland cement concretes. The rate at which concrete carbonates is determined by its permeability, degree of saturation with water, and the mass of calcium hydroxide available for reaction. Well-compacted and properly cured concrete, at a low water-to-cement ratio, will be sufficiently impermeable to resist the advance of carbonation beyond the first few millimetres.

If carbonation progresses into a mass of concrete, three deleterious consequences may follow:

— Permeability may increase.

— Shrinkage may occur.

— Carbonation of the concrete immediately adjacent to steel reinforcement may reduce its resistance to corrosion.

In 1968, results from long-term investigations of concrete in Japan were reported (156,157) indicating that concrete made with blended cements was subject to more rapid carbonation than normal portland cement concrete. Other investigations (158–160) have not shown any appreciable differences in this regard, provided that the strength of the concretes being compared is equal.

In 1980, Tsukayama et al. (161) reported data from experiments conducted over a long period on fly ash concretes exposed in the field in Japan.

They found that the depth of carbonation (termed *neutralization* by the authors) was found to be related to the quality of the concrete in the following ways:

— A linear relationship was found between water-to-cement ratio (excluding fly ash) and depth of neutralization.

— At identical water-to-cement ratios, when fly ash was added, depth of carbonation was found to be slightly decreased.

- The period of curing in water, after casting the specimens, was found to have a substantial influence on concrete exposed indoors. Concrete exposed outdoors was adequately cured after about one week in water.

Gebauer (162) examined slabs of steel-reinforced concretes formed by compaction and vibration. They were cured for seven days at 20°C and 95% RH. Subsequently, one slab of each composition was placed in an outdoor testing station; control slabs were kept under moist-curing conditions (indoor slabs). The compressive strengths of companion prisms were measured at 28 and 365 days.

Gebauer reported that carbonation depth increased as:

- strength and pulse velocity decreased (regardless of composition);
- water-to-cement ratio increased;
- cement content decreased;
- fly ash content increased.

The primary correlation was found to be between carbonation depth and compressive strength (determined on cores of the slabs, not on test prisms).

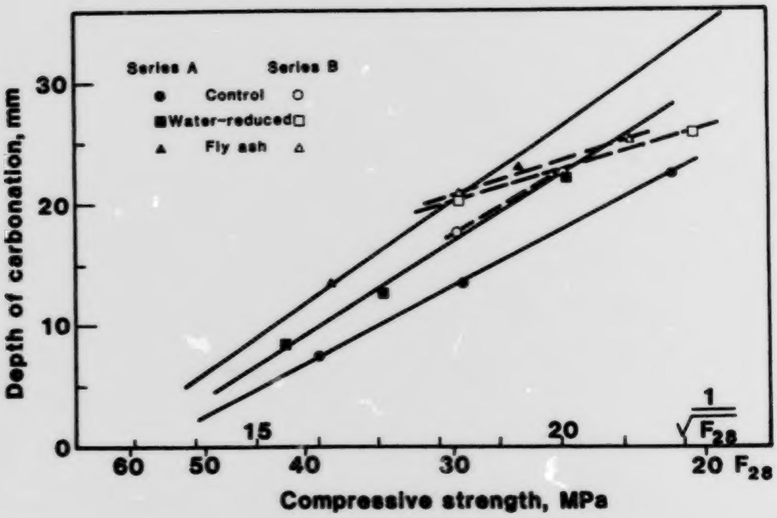

Fig. 7.1 — Depth of carbonation versus compressive strength of fly ash concretes (accelerated testing) (163)

Ho and Lewis (163) examined the rates of carbonation of three types of concrete (plain, water-reduced, and fly ash) at equal slump. Accelerated carbonation was induced by storing specimens in an enriched CO_2 atmosphere (4%) at 20°C and 50% RH for eight weeks. The authors note that one week under these conditions is about equivalent to one year in a normal atmosphere (0.03% CO_2).

The data from this study are presented in Figure 7.1 in terms of depth of carbonation versus 28-day compressive strength.

It is clear that there is an inverse relationship between strength and depth of carbonation and that the fly ash concrete was more readily carbonated than the non-fly ash concrete, especially at lower strengths (<30 MPa).

Depth of carbonation versus cement content is shown in Figure 7.2 as a function of time of moist-curing.

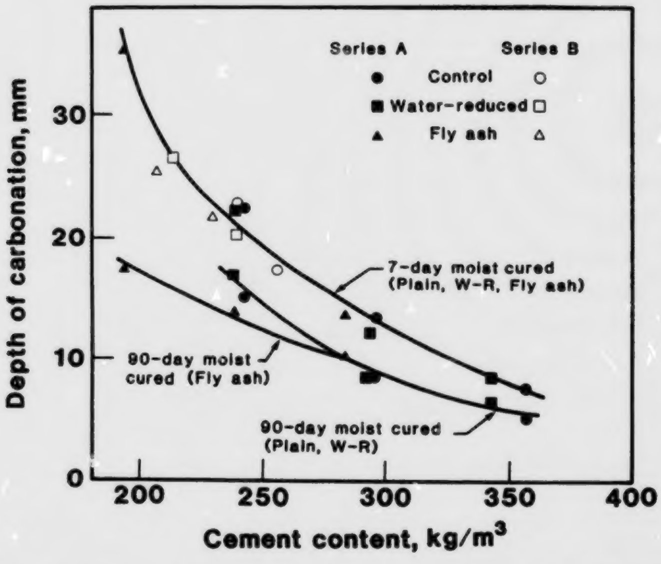

Fig. 7.2 — Depth of carbonation versus cement content of fly ash concretes (accelerated testing) (163)

The authors concluded as follows:

- Concretes having the same strength and water-to-cement ratio do not necessarily carbonate at the same rate.
- Based on a common 28-day strength, concrete containing fly ash showed a significant improvement in quality when curing was extended from 7 to 90 days. Such improvement was much greater than that achieved for the plain concrete.

- The depth of carbonation is a function of the cement content for concretes moist-cured for seven days. However, with a further curing to 90 days, concrete containing fly ash showed a slower rate of carbonation as compared to plain and water-reduced concretes.

There is no doubt that these conclusions are consistent with the reported observations. However, the approach taken in this research has a major weakness, the influence of which must not be disregarded. In the accelerated test, concrete specimens that have been moist-cured for 7 days, conditioned in the laboratory for 21 days at 20°C and 50% RH, are exposed to CO_2 (at elevated pressure) for eight weeks. The age of the concrete at the start of the test is 28 days. Its maturity, however, is considerably less than an equivalent 28-day moist-cured concrete (although it is arguable that it is closer to the condition of *real* concrete in most construction situations). The concrete is exposed to a rate of carbonation at least five times that of atmospheric exposure while at the same time being kept at 50% RH (163). The disparity between the rate of carbonation and the rate of maturing is extreme and becomes greater the longer the experiment proceeds.

As Buttler et al. (164) have noted, the accelerated test may be capable of application to different cements with different mix proportions. It is not applicable when comparing concretes made with portland cement with those made with blended cements because of the slow rate of pozzolanic reactions.

In general, it appears that good-quality fly ash concrete is comparable to plain concrete in its resistance to carbonation. If concrete is placed at a low cement factor, with insufficient curing (either lack of moisture or low temperature), it should come as no surprise to find that it is not durable to all forms of chemical and physical aggression, including carbonation.

Effects of Fly Ash on the Durability of Concrete to Repeated Cycles of Freezing and Thawing

It is now generally accepted, other criteria also being met, that air-entrainment renders concrete frost-resistant. As was discussed in Section 3 of this chapter, fly ashes, in common with other finely divided mineral components in concrete, tend to cause an increase in the quantity of admixture required to obtain specified levels of entrained air in concrete. In some instances, the stability or rate of air loss from fresh concrete is also affected. In general, the observed effects of fly ash on freezing and thawing durability support the view expressed by Larson (69):

> "... Fly ash has no apparent ill effects on the air voids in hardened concrete. When a proper volume of air is entrained characteristics of the void system meet generally accepted criteria."

Gebler and Klieger (76) extended their study of air-entrainment of fly ash concrete (see Section 3) to include an examination of the air-void parameters of hardened concretes cast after initial mixing, and after 30, 60, and 90 minutes. From these experiments the authors concluded as follows:

> "Spacing factors ($\bar{L}$) of specimens cast over a period of 90 minutes were essentially constant for the majority of concretes containing fly ash. In addition, the initial spread of results of specific surface and voids per inch was essentially similar for concretes containing Class F or Class C ash. However, when measured on specimens cast at 90 min., concretes with Class F ash exhibited greater variability of results for these air-void parameters than concretes with Class C ash."

Sturrup, Hooton, and Clendenning (165), related the freezing and thawing performance of low-calcium fly ash concretes to carbon content. Accelerated freezing and thawing tests (ASTM C 666, Procedure A) and outdoor exposure tests were conducted on concrete specimens containing low-calcium ashes of 5.4, 12.3, and 23% carbon, at 15, 30, 45, and 60% replacement of cement by weight. Water-to-cement-plus-fly ash ratios were kept constant at 0.6 and with the exception of a specimen at 23% carbon (air content = 3.6%) air content was kept at 6.5 ± 1%.

It was reported that correlation between durability factor, as determined by resonant frequency, and carbon content was poor; correlation with weight loss resulting from freezing and thawing cycling was more definite. This was taken to indicate that surface scaling, rather than internal damage, was the result of frost action on the specimens (166). This was confirmed by observation of outdoor exposed specimens (167).

Yuan and Cook (83) have reported on the freezing and thawing resistance of concrete incorporating high-calcium fly ash. Two series of concrete specimens (non-air-entrained, air-entrained) were examined with 0, 20, 30, and 50% replacement of cement by weight. Yuan and Cook made the following observations:

- — The superior freezing and thawing resistance of air-entrained concrete is evident with or without fly ash replacement.
- — The concrete with 20% of fly ash was found to be more durable than the control.
- — As the quantity of fly ash in air-entrained concrete was increased to 50%, more scaling damage was noted after 400 cycles.

The freezing and thawing resistance of fly ash concretes incorporating both low- and high-calcium fly ashes was determined in the CANMET study (38). Table 7.3 shows the durability factors found for specimens made from the concretes described elsewhere in this chapter (see Tables 3.2 and 4.1, Sections 3 and 4, respectively).

Table 7.3 — Freeze–thaw durability factors for fly ash concretes*

Mixture no.	Air content, %	Durability factor after 300 cycles, %**
Control 1	6.5	97.7
Control 2	6.4	98.1
F1	6.2	96.4
F2	6.2	98.8
F3	6.2	96.8
F4	6.3	98.8
F5	6.4	97.2
F6	6.5	96.8
F7	6.1	97.6
F8	6.2	96.9
F9	6.4	97.6
F10	6.5	97.2
F11	6.6	95.8

*From reference 38.

**Determined in accordance with ASTM C-666 (Procedure A).

Virtanen (81) compared the freezing and thawing resistance of fly ash, condensed silica fume, and slag concretes. An estimate was made of the relative *theoretical service life* for each type of concrete as a function of air content (Fig. 7.3) and the author made the following observations:

— "The air content has the greatest influence on the freeze–thaw resistance of concrete.

— "Addition of fly ash has no major effect on the freeze–thaw resistance of concrete if the strength and air content are kept constant.

— "The addition of blast-furnace slag or fly ash may have a negative effect on the freeze–thaw resistance of concrete when a major part of the cement is replaced by them."

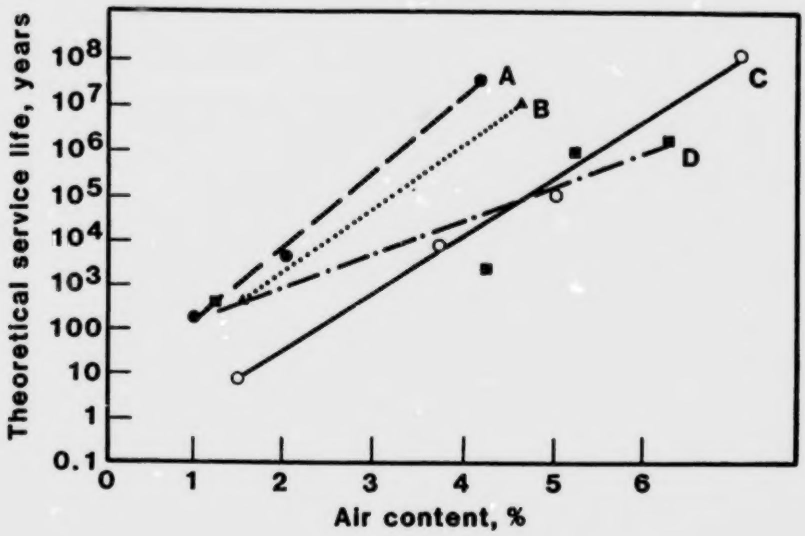

Fig. 7.3 — Relationship between theoretical service life and air content of fresh concrete (81)

Key: A — Concretes incorporating ground, granulated blast-furnace slag

B — Concretes incorporating condensed silica fume

C — Control concretes

D — Concretes incorporating fly ash

Larson (69), discussing some of the difficulties of interpreting the findings of much of the early work on freezing and thawing resistance of fly ash concrete, made the following observation:

> "Fly ash concrete durability characteristics are influenced and obscured by all the factors operating on ordinary concrete. They are also related to variations in the fly ash itself and perhaps to the associated phenomenon of increased air-entraining-agent requirement. When valid comparisons are made with equal strengths and air contents, however, there are no apparent differences in the freezing and thawing durability of fly-ash and non fly-ash concretes."

Another aspect of freezing and thawing testing procedure has been criticized by Brown et al. (168) who made the following comments on freezing and thawing testing of blended cements:

> — "When blended cements are tested according to ASTM C 666-73, the standard method for measuring the freezing and thawing durability of portland cement concretes, inferior resistance is usually observed. This is probably because test initiation after only a short curing period does not make proper allowance for the generally lower rate of strength development of blended cements.
>
> — "Freezing and thawing studies, when initiated after longer curing periods, have indicated that blended cements, due to development of strengths equivalent or superior to those of portland cements, also develop superior resistance to freezing and thawing."

These points should certainly be kept in mind when consideration is being given to reports of all aspects of the durability of fly ash concrete, not merely to its frost resistance.

Effects of Fly Ash on Durability of Concrete Exposed to Elevated Temperatures

The influence of elevated temperatures on the strength of concrete during curing has been discussed at some length in Section 4 of this chapter. In recent years, the use of concrete in structures required to withstand elevated temperatures under some circumstances (such as nuclear reactor containment structures) has generated renewed interest in the effects of high temperatures on fly ash and other concretes.

Nasser and Lhotia (169,170) and Nasser and Marzouk (103,171) have studied plain and fly ash concretes at temperatures up to 230°C. Carette, Painter, and Malhotra (172) have studied concretes with normal portland cement, slag, and fly ash at sustained temperatures up to 600°C. Data from this research are shown in Figure 7.4. In general, the incorporation of fly ash appears not to influence the behaviour of concrete at elevated temperatures. Loss of strength and changes in other structural properties occur at about the same temperatures for both types of concrete.

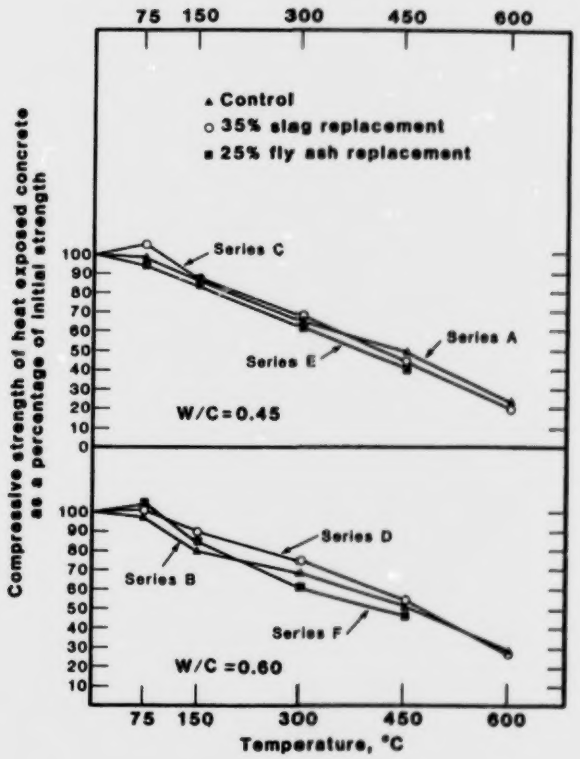

Fig. 7.4 — Compressive strength of concretes after one month of exposure to various elevated temperatures (172)

Abrasion and Erosion of Fly Ash Concrete

Under many circumstances, concrete is subjected to wear by attrition, scraping, or the sliding action of vehicles and other objects. When water flows over concrete surfaces, erosion may occur. In general, regardless of the type of test performed, the abrasion resistance of concrete is usually found to be proportional to its compressive strength (94). Similarly, at constant slump, resistance to erosion improves with increased cement content and strength. It may be anticipated that fly ash concrete that is incompletely or inadequately cured may show reduced resistance to abrasion.

Liu (173) has examined the abrasion–erosion resistance of concrete using a newly developed underwater abrasion test. One of the concrete mixes examined by Liu incorporated fly ash at 25% by volume replacement for portland cement. Details of the type and origin of the fly ash used were not reported. Performance of the fly ash concrete, cured for 90 days to an average compressive strength of 49 MPa (7170 psi), was compared with a concrete of similar mix proportions, containing no fly ash, cured for 28 days, with an average compressive strength of 47 MPa (6870 psi).

Little difference in abrasion resistance was found between the two concretes for test periods up to 36 hours. At prolonged test times, the performance of the fly ash concrete was inferior to that of the control. After 72 hours, the fly ash concrete had lost almost 25% more mass (7.6% loss) due to abrasion-erosion than the control (6.1% loss).

At present, insufficient information is available to establish any relationship between abrasion and fly ash use, beyond that of the influence of fly ash on strength development in concretes. The resistance of fly ash concretes to erosion and abrasion under many forms of exposure urgently requires research.

Effects of Fly Ash on Durability of Concrete Exposed to Chemical Attack

Introducing fly ash as a component of concrete has been shown to influence its durability to chemical attack. Leaching of calcium hydroxide, acidic dissolution of cementitious hydrates, the action of atmospheric and dissolved carbon dioxide, and the reactivity of cement components to ions in solution are the main causes of deterioration of concrete exposed to chemical action.

Biczok (174) enumerates four conditions related to concrete quality and the constituents of concrete upon which the destructive effects of aggressive waters depend:

1. type of cement used, its chemical and physical properties;
2. quality of concrete aggregates, their physical properties and gradation;
3. method used for preparing concrete, the water-to-cement ratio, the proportion of cement, the placement;
4. condition of the surface exposed to the water.

Of these, condition 1 relates strictly to the nature of the cementitious binder used, whereas conditions 2, 3, and 4 may be grouped under one or more aspects of the permeability of concrete.

With regard to cement type, two factors are influential in determining the relative durability of fly ash concrete:

- — The chemical composition of the cement, vis-à-vis the cementitious components produced during hydration, has a pronounced influence on the durability with respect to chemical action. The most notable example is the use of low-C_3A, (ASTM Type V) cements as a means of controlling attack due to sulphate ions.
- — A combination of chemical composition and physical properties, notably fineness, determines the rate at which cement hydration proceeds and, at least for the early life of a structure, must influence its permeability.

Fly ash, used as a replacement for portland cement, has an indirect influence on both factors. At early ages, it serves only as an inert component and is therefore similar to reduction in cement content. At later ages, it contributes to the formation of cementitious components but, as Kovacs (175) has shown, it does so in a manner that changes the relative proportions of the usual hydrate materials. Finally, it converts some of the calcium hydroxide, which is produced when cement hydrates, to less reactive calcium silicates and aluminates,

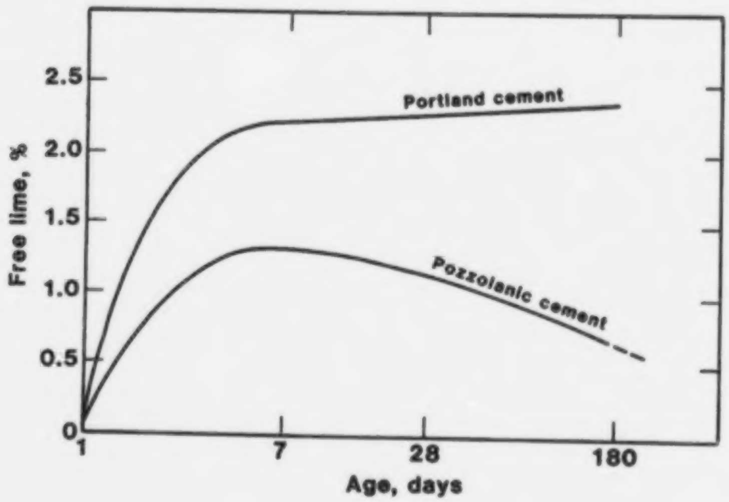

Fig. 7.5 — Free lime content of 1:3 cement sand mortars (176)

through the pozzolanic reaction. The removal of free calcium hydroxide by reactive combination with pozzolans was shown by Lea (176) to progress as is illustrated in Figure 7.5, in which the quantity of free $Ca(OH)_2$ in mortars made with and without pozzolan is compared as a function of age. It is generally considered that in concrete this process leads to long-term gains in watertightness, strength, and resistance to aggressive environments.

Except for general recognition of this final point, there seems to have been little consideration given in the research literature to the role played by fly ash in changing the chemical balance of the cementitious components of concrete, either as a factor in concrete durability or in respect to the development of test methods.

Effects of Fly Ash on Sulphate Resistance of Concrete

In 1937, Davis et al. (2), reported that some fly ashes increased the resistance of concrete to sulphate attack, others were ineffective, and some were deleterious and caused increased sulphate deterioration.

In 1967, Dikeou (177) reported the results of sulphate resistance studies on a total of 30 concrete mixes made from 3 portland cements, 3 portland–fly ash cements, and 12 fly ashes. From this work it was concluded that all of the fly ashes tested greatly improved sulphate resistance. The relative order of improvement found in this investigation is shown in Figure 7.6.

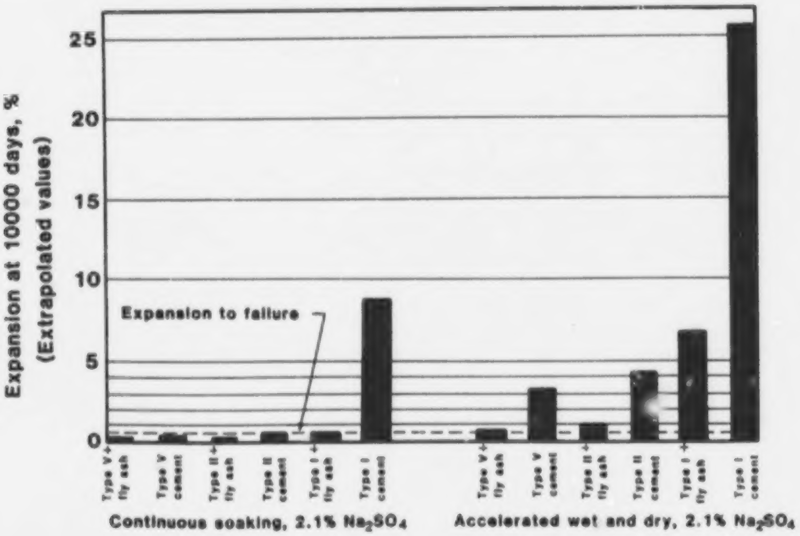

Fig. 7.6 — Sulphate expansion of concretes containing 30% of fly ash (177)

Kalousek, Porter, and Benton (178) reported studies on the requirements of concrete for long-term service when exposed to sulphate. From this work they concluded that:

- Eighty-four per cent of the ASTM Types V and II cement concretes without pozzolan showed a life expectancy of less than 50 years.
- Certain pozzolans increased very significantly the life expectancy of concrete exposed to 2.1% sodium sulphate solution. Fly ashes meeting present-day specifications were prominent among the group of pozzolans showing the largest improvements.
- Concretes for long-term survival in a sulphate environment should be made with high-quality pozzolans and a sulphate-resisting cement. The pozzolan should not increase significantly, but preferably decrease, the amount of water required.
- Cement to be used in making sulphate-resisting concrete with pozzolan of proven performance should have a maximum C_3A content of 6.5% and maximum C_4AF content of 12%. Restrictions of cements to those meeting present-day specifications for Type V cement does not appear justified.

The fly ash samples examined by Dikeou (177) and those examined by Kalousek et al. (178) originated from bituminous coals.

In 1976, Dunstan (179) reported the results of experiments on a total of 13 concrete mixes made using fly ashes from lignite or subbituminous coal sources. On the basis of this work he concluded that lignite and subbituminous fly ash concrete generally exhibited reduced resistance to sulphate attack.

Dunstan's work was extended and in 1980 a report (180) was published summarizing the results of a five-year study on sulphate attack on fly ash concretes. This report includes a theoretical analysis of sulphate attack and its causes. The basic postulate of Dunstan's thesis is that CaO and Fe_2O_3 in fly ash are the main contributors to the resistance or susceptibility of fly ash concrete to sulphates. Dunstan notes that as the calcium oxide content of ash increases above a lower limit of 5%, or as the ferric oxide content decreases, sulphate resistance is reduced. To use this observation as a means to select potentially sulphate-resistant fly ashes (or, more important, fly ashes that can improve the sulphate resistance of concrete), Dunstan proposed the use of a resistance factor (R) calculated as follows:

$$R = (C-5)/F$$

where:

C = per cent CaO
F = per cent Fe_2O_3.

Figures 7.7 and 7.8 show the results from two types of laboratory sulphate-resistance tests on samples of concretes containing high-calcium fly ashes with the properties shown in Table 7.4. Figures 7.9 and 7.10 show the results from similar tests on samples of concretes containing low-calcium fly ashes with the properties also shown in Table 7.4. The influences (positive and negative) of fly ash are clearly seen from these data.

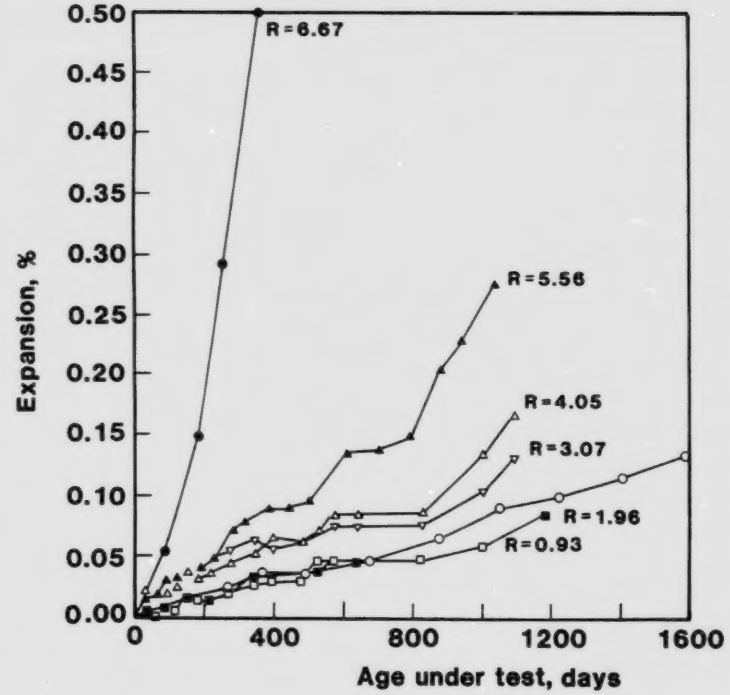

Fig. 7.7 — Sulphate expansion of concretes containing high-calcium fly ash (soak test) (180)

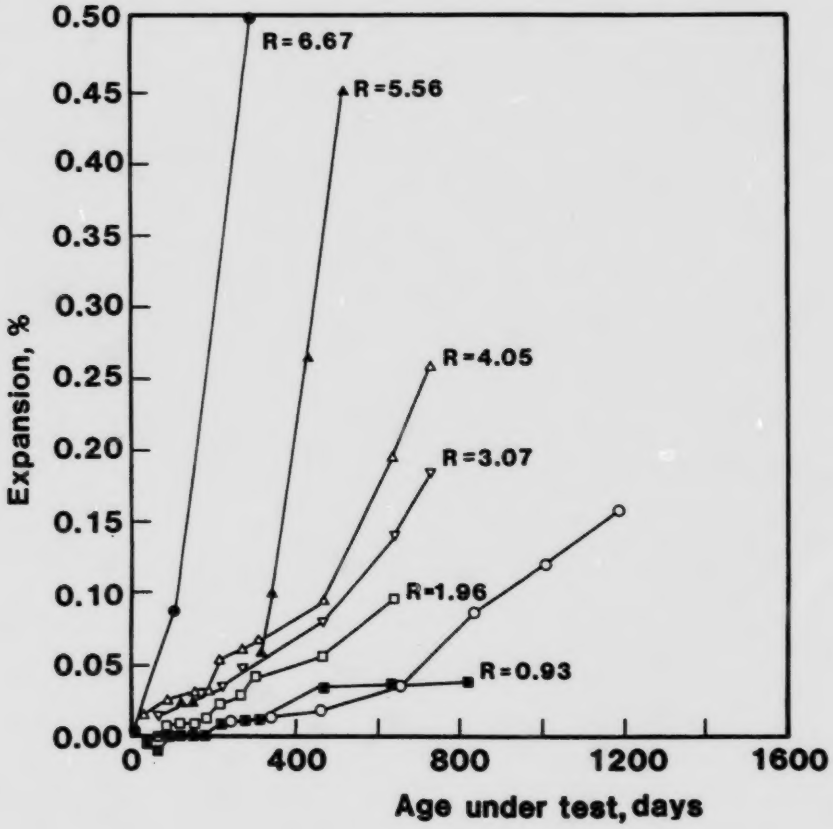

Fig. 7.8 — Sulphate expansion of concretes containing high-calcium fly ash (wet/dry test) (180)

Table 7.4 — Characteristics of fly ashes examined by Dunstan*

	Composition, mass %							
Fly ash #	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	SO_3	Alkali	LOI
M-6498	46.1	19.0	18.6	8.2	1.3	1.6	0.72	2.0
M-6535	28.1	20.0	4.1	32.0	6.4	3.8	0.68	0.2
M-6734	34.7	24.8	4.2	26.1	5.2	1.4	0.81	0.2
M-6514	37.2	15.6	5.6	24.3	11.3	0.9	0.07	0.3
M-6510	37.1	11.8	7.3	21.8	5.6	2.6	4.23	0.3
M-6577	31.1	17.1	7.9	25.3	8.1	3.3	1.35	1.1
M-6569	51.8	27.2	2.0	10.7	2.1	0.7	0.86	1.2
M-6730	49.6	25.7	3.0	11.3	2.1	0.7	1.20	1.3
M-6754	61.4	23.4	3.7	7.0	1.2	0.5	0.81	2.5
M-6679	32.8	19.6	4.1	28.0	5.5	3.4	1.54	0.5
M-6680	36.9	18.1	4.7	24.0	4.8	2.8	1.86	0.6
M-6681	41.1	17.9	4.9	20.2	4.4	2.2	2.21	0.8
M-6682	45.7	18.4	5.3	15.5	3.8	1.6	2.83	0.9
M-6683	51.5	24.5	5.7	10.2	2.1	0.9	0.96	1.2
M-6734	34.7	24.8	4.2	26.1	5.2	1.4	0.81	0.2

*From references 66, 180.

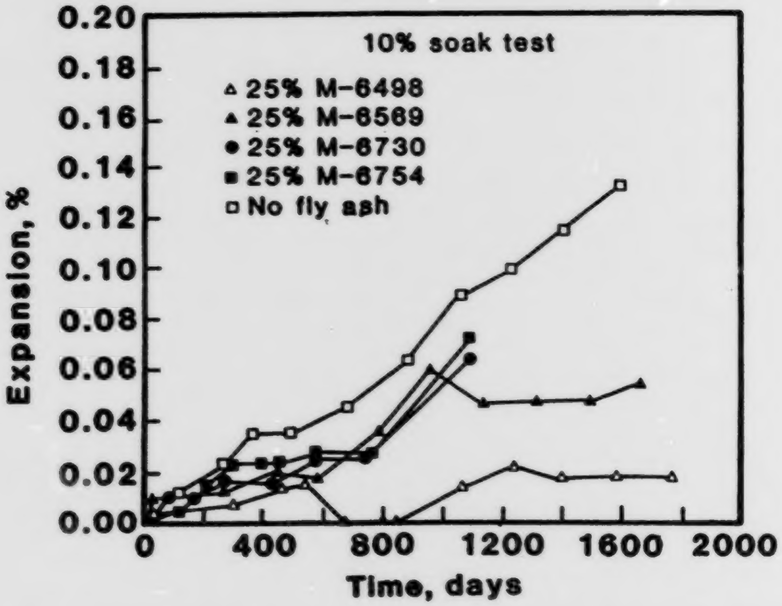

Fig. 7.9 — Sulphate expansion of concretes containing low-calcium fly ash (soak test) (179)

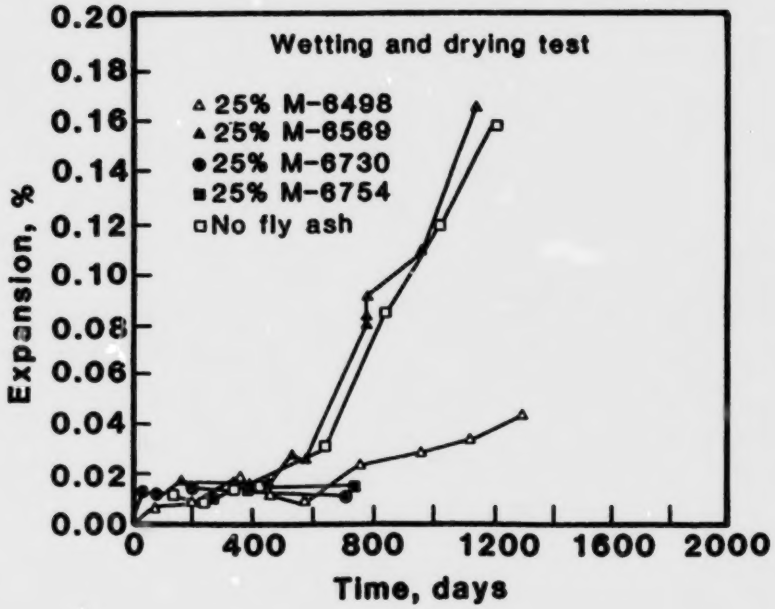

Fig. 7.10 — Sulphate expansion of concretes containing low-calcium fly ash (wet/dry test) (179)

The findings of Dunstan's work have been summarized in terms of the selection of fly ashes for sulphate-resistant concrete as follows:

R Limits*	Sulphate Resistance**
< 0.75	Greatly improved
0.75 to 1.5	Moderately improved
1.5 to 3.0	No significant change
>3.0	Reduced

The U.S. Bureau of Reclamation has incorporated a more conservative (181) version of Dunstan's limits into a recently revised reprint of the *Concrete Manual* (182), details of which are given in Table 7.5.

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*At 25% cement replacement.

**Relative to ASTM Type II cement at 0.45 W/C.

Table 7.5 — Bureau of Reclamation cementitious materials options for sulphate resistance*

I. Positive Sulphate Attack (0.10–0.2% or 150–1500 ppm)
  A. Type II cement
  B. Type II cement plus class N,F, or C pozzolan
    with R less than 2.5
  C. Type IP (MS) cement
    with R less than 2.5

II. Severe Sulphate Attack (0.2–2% or 1500–10,000 ppm)
  A. Type V cement
  B. Type V cement plus class N,F, or C pozzolan
    with R less than 2.5
  C. Type II cement plus class N,F, or C pozzolan
    with R less than 2.5
  D. Type IP (MS) cement
    with R less than 2.5 if C_3A less than 5.0
    with R less than 1.5 if C_3A between 5.0 and 8.0

III. Very Severe Sulphate Attack (2% or more or >10,000 ppm)
  A. Type V cement plus class N,F, or C pozzolan
    with R less than 1.5
  B. Type II cement plus class N,F, or C pozzolan
    with R less than 0.75
  D. Type IP (MS) cement
    with R less than 1.5 if C_3A less than 5.0
    with R less than 0.75 if C_3A between 5.0 and 8.0

*From reference 181.

Mather (183) has reported data from two studies in progress at the laboratories of the U.S. Corps of Engineers in which various pozzolans are under investigation for their influence on sulphate resistance of concrete. The data presented were obtained from exposure of mortars to 0.352 molar Na_2SO_4 solution. Care was taken in the experiments to expose the mortar bars to sulphate solutions only after they had reached about equal maturity, as determined by measurements of compressive strength on companion mortar cubes.

Three non-sulphate-resisting cements were used, with C_3A contents of 14.6% (cement RC-756), 13.1% (cement RC-714), and 9.4% (cement RC-744), respectively. Ten pozzolans were examined, comprising one condensed silica fume, one volcanic glass, three fly ashes of subbituminous origin, one bituminous fly ash, and four fly ashes from lignite coals. It is unfortunate that the chemical and physical properties of these materials are not recorded in this preliminary report of the study.

The pozzolans were incorporated in mortars by replacement of 30% (by volume) of portland cement.

Figure 7.11 shows some of the results obtained from these experiments. The ranking of effectiveness in reducing sulphate expansion was found to be, from best to worst, as follows: condensed silica fume, volcanic glass, sub-bituminous fly ash (three examples), bituminous fly ash, and lignite fly ash (four examples).

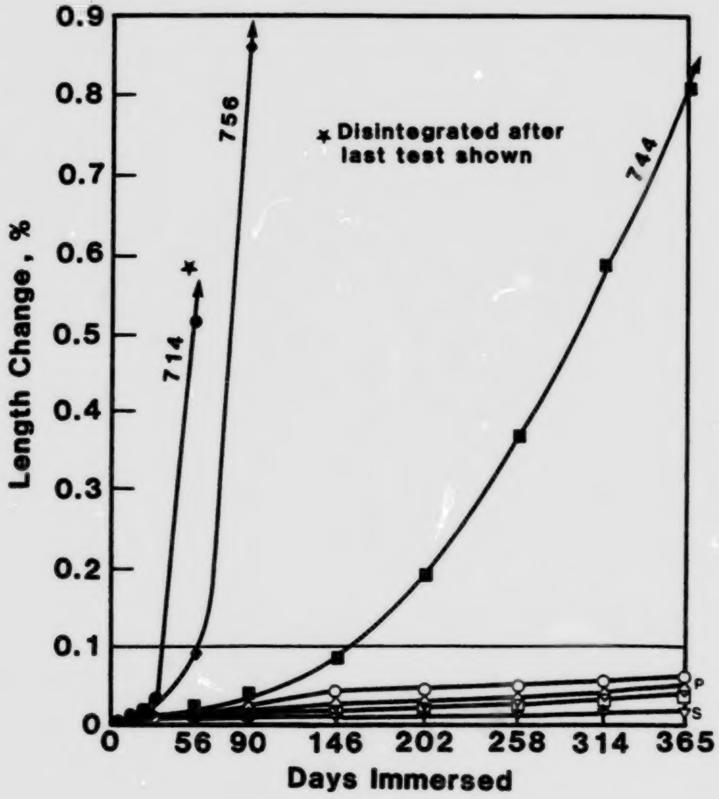

Fig. 7.11 — Effects of condensed silica fume and volcanic glass pozzolan on expansion of mortar prisms incorporating non-sulphate-resisting cement in sulphate solution (183)

Key: *714 = Cement with calculated C_3A, 13.1%*
756 = Cement with calculated C_3A, 14.6%
744 = Cement with calculated C_3A, 9.4%
S = 30% replacement of cement by condensed silica fume.
P = replacement of cement by pozzolan.

Mather summarized the findings of the study-in-progress as follows:

> "... what seems to be suggested (by the results) is that a pozzolan of high fineness, high silica content and highly amorphous silica is the most effective pozzolan for reducing expansion due to sulphate attack on mortars made with non-sulphate resisting cements... The pozzolans that resulted in poorer performance ... were in 6 of 7 cases fly ashes produced by the combustion of lignite."

It might be added that the ranking of subbituminous ashes as better than the one bituminous ash examined is in direct contradiction with the findings of Dunstan (179,180). However, in the absence of detailed properties of the ashes examined and without comparable data from mortars made with other fly ashes, it would not be advisable to draw further conclusions from this report. Clearly, the influence of fly ash on the sulphate resistance of concrete is not completely understood, and much more research should be conducted to establish guidelines on this important aspect of concrete durability.

Effects of Fly Ash on Alkali–Aggregate Reactions in Concrete

Shortly after he discovered that alkali–aggregate reactivity was a cause of expansion and damage in some concretes, Stanton (184) reported that the effects could be reduced by adding finely ground reactive materials to the concrete mix. Subsequently, a variety of natural and artificial pozzolans and mineral admixtures, including fly ash, have been found to be effective in reducing the damage caused by alkali–aggregate reactions (AAR). As discussed below, the effectiveness of fly ash (and other mineral admixtures) in controlling AAR appears to be limited to reactions involving siliceous aggregates. A second form of alkali–aggregate reaction, alkali–carbonate reaction, has been reported (185) and has been shown to be relatively unresponsive to control by the addition of pozzolans (186).

It is not within the scope of this review to consider the many and complex aspects of AAR; these matters are the subject of much current research and are poorly understood. Rather, consideration has been limited in this review to some aspects of the subject directly relevant to the selection of fly ash as a means to control alkali–silica reactivity.

The effectiveness of fly ash in the control of alkali–silica reactivity has been widely reported. Pepper and Mather (187) reported the minimum percentage replacement (by volume) of cement by fly ash required to reduce expansion in test specimens by 75%. Their results are shown in Table 7.6.

Table 7.6 — Mimimum percentage replacement of fly ash*

Replacement material	Minimum percentage (by volume) replacement for effectiveness		
	14 days	6 months	average
Fly ash I	46	36	41
Fly ash II	48	36	42
Fly ash III	52	36	44
Fly ash IV	45	34	40

*From reference 187.

Elfert (62) reported data of a similar nature from work carried out at the U.S. Bureau of Reclamation (Figure 7.12).

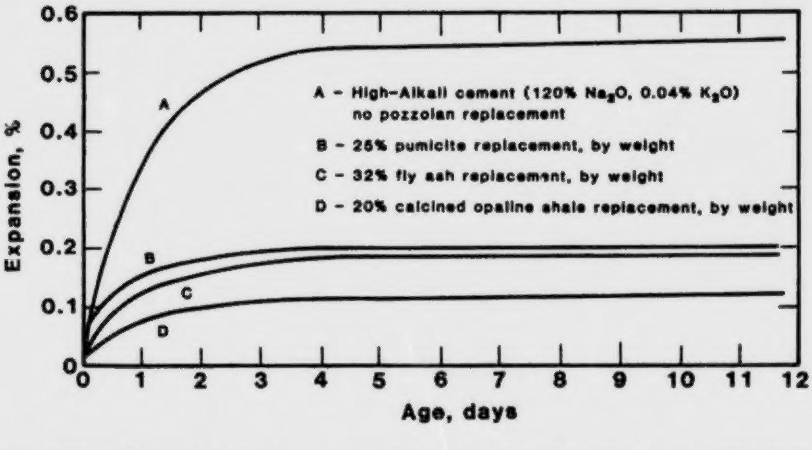

Fig. 7.12 — Effect of pozzolan on reactive expansion of mortar made with alkali cement and crushed Pyrex glass (62)

Although it is clear that some fly ashes are effective in controlling alkali–aggregate expansion, it is questionable whether the early strength losses caused by replacement of 40 to 50% of the cement by low-calcium fly ash would be tolerable for more than a limited number of applications. Similar levels of replacement using high-calcium fly ashes may be more acceptable.

During a study of alkali-reactive aggregates in Nova Scotia, Duncan et al. (188) showed effective suppression of expansion by replacement of moderate alkali cement — 0.71% as Na_2O — with as little as 25% of fly ash.

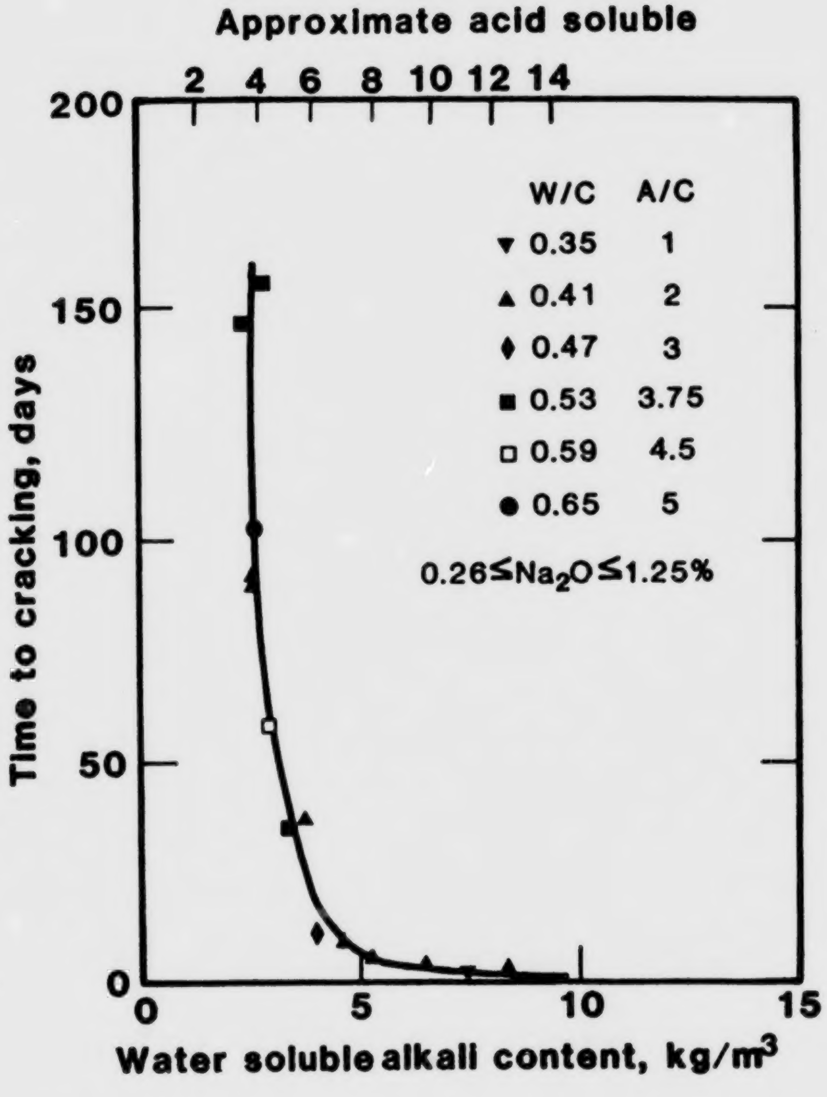

Fig. 7.13 — Variation in time to cracking with water-soluble alkali content at the most critical alkali–Beltane opal ratio (189)

In more recent studies, the following factors have been identified as particularly important:

- the concentration of soluble alkali in the system;
- the type of aggregate;
- the quantity of fly ash used.

It is now generally accepted that, with regard to alkali–silica reactivity, it is the concentration of soluble alkali, rather than the total alkali content of the system that affects expansion. Figure 7.13 shows the relationship between water soluble alkali content and the time required for cracking in concrete containing Beltane opal as aggregate, as reported by Hobbs (189).

In general, Hobbs estimated that the lower limit of alkali concentration at which mortar test specimens exhibit excessive cracking was 3.4 kg/m^3 as acid-soluble alkali (190). This is equivalent to 2.5 kg/m^3 as water-soluble alkali (189).

The source of alkali (as Na_2O or K_2O) is not regarded as important. Thus soluble alkali from fly ash is regarded as equally deleterious as that from portland cement. This is particularly important with regard to the use of high-calcium fly ashes containing large amounts of soluble alkali sulphates. These have been reported (93) to increase rather than decrease the rate of deterioration through alkali–silica reactivity.

Not all aggregates are susceptible to alkali–silica reactivity nor do all susceptible aggregates behave in the same way. Alkali–silica reactivity is a long-term process that has been found to occur most commonly with aggregates that contain non-crystalline or crypto-crystalline silica.

Aggregates and their mineralogical constituents known to react with alkalis in concrete include (191):

- the silica materials: opal, chalcedony, tridymite, cristobalite;
- zeolite;
- heulandite;
- glassy to crypto-crystalline rhyolites, dacites, andesites and their tuffs;
- certain phyllites.

In Britain, the main reactive component of aggregates susceptible to alkali–silica reactivity has been found to be chert (flint) (192). In South Africa, studies have been made on hornfels of the Malmesbury Group (193).

Much of the experimental work in the literature has been directed to the study of very reactive, porous, opaline aggregates, such as the Beltane opal from California, or to Pyrex glass. Both are generally more reactive than many of the natural aggregates encountered in practice, and this should be considered when the reported data are being evaluated from the perspective of practical applications.

As with most other aspects of fly ash utilization, ashes from different sources behave significantly differently in their effects on alkali–silica reactivity. As was noted above, some high-calcium fly ashes have been found in the laboratory to be ineffective or deleterious in relation to alkali reactivity.

In studies using Beltane opal, Hobbs (194) reported the data shown in Figure 7.14 for fly ashes with the chemical compositions summarized in Table 7.7. The following conclusions were drawn by the author from these experiments:

— "The partial replacement of a high-alkali cement by fly ash reduced the long-term expansion due to alkali-silica reactivity but, even when 30 or 40% of the cement was replaced, most of the blended cement mortars cracked at earlier or similar ages to the portland cement mortars.

— "The effectiveness of the fly ashes in reducing long term expansion varied widely. It is suggested that the effectiveness of the (fly ashes) may be dependent upon their alkali content or fineness.

— "Where part of the cement was replaced by fly ash, the lowest mortar alkali content, expressed as equivalent Na_2O, at which cracking was observed was 2.85 kg/m^3. This figure relates only to the acid soluble alkalis contributed by the portland cement and compares with a figure of 3.5 kg/m^3 for a portland cement mortar.

— "If it is assumed that fly ash acts effectively like a cement with an alkali content of 0.2% by weight, the lowest alkali content at which cracking was observed was 3.4 kg/m^3.

— "Both fly ashes and granulated blast furnace slags act as alkali diluters, slags being more effective in reducing damage due to alkali-silica reactivity than fly ash.

— "From the above it may be concluded that, when the aggregate to be used contains a reactive constituent and when the concrete is to be exposed to external moisture, damage due to alkali-silica reactivity is unlikely to occur if the acid-soluble equivalent Na_2O content of the concrete is below 3 kg/m^3. In calculating the alkali content of the concrete, granulated blast furnace slags may be assumed to contain no available alkalis but fly ash should be assumed to have an available alkali content of 0.2% by weight."

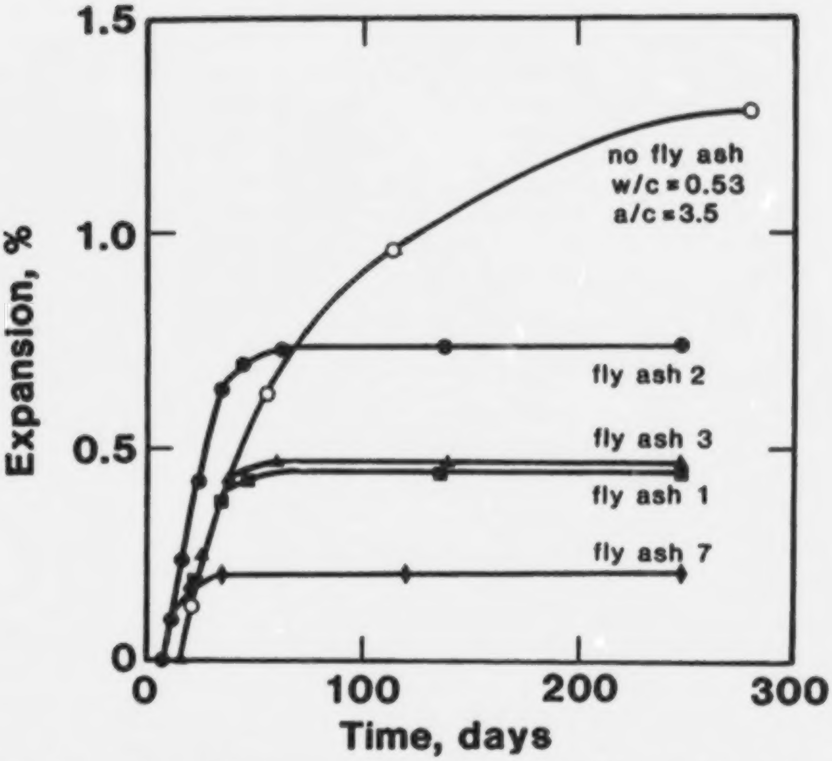

Fig. 7.14 — Variation in expansion with age for specimens where part of the aggregate was replaced with fly ash (194)

Table 7.7 — Composition and properties of fly ashes examined by Hobbs*

	Fly ash number			
Composition, %	1	2	3	7
SiO_2	50.02	51.48	46.58	49.72
Fe_2O_3	9.02	8.70	14.24	5.22
Al_2O_3	26.83	28.08	25.22	32.45
CaO	1.48	1.27	4.10	2.77
MgO	0.93	0.93	0.95	2.41
SO_3	0.79	1.15	1.29	0.53
LOI	3.43	1.74	1.84	3.24
Na_2O (total)	0.88	1.13	0.80	0.38
Na_2O (water sol.)	0.07	0.10	0.08	0.02
K_2O (total)	3.90	3.85	2.35	1.40
K_2O (water sol.)	0.07	0.11	0.04	0.02

*From reference 194.

From experiments using Pyrex glass, Nixon and Gaze (192) drew the following conclusions:

- "When Pyrex glass is used as the reactive aggregate the partial replacement of a high alkali portland cement by fly ash or by granulated blast furnace slag produces a significant reduction in expansion of mortar bars at all replacement levels tested (10, 20 and 30 per cent fly ash). The reductions are greater than could be accounted for by simple dilution of the alkali content of the portland cement.
- "Weight for weight the fly ashes are more effective (than granulated slag) in reducing expansion ...
- "Only small differences were found between the effectiveness of different fly ashes. These differences could best be correlated with a measure of the pozzolanicity of the ash. The ashes with lower alkali content did, on the whole, seem to perform slightly better than those with high alkali (content) but this effect was secondary to the pozzolanicity. The available alkali content of the ashes gave no better correlation with the observed expansions than did the total alkali content ...."

The same authors (195) reported on studies using chert aggregate in fly ash concrete prism specimens and presented the data shown in Figure 7.15.

Oberholster and Westra (193) studied alkali–silica reactivity in the Malmesbury Group aggregates and examined, among many additives, a low-calcium fly ash. The authors reported the fly ash to be more effective in reducing expansion than would be expected for a simple dilution of alkali content.

The study by Oberholster and Westra (193) included an examination of concrete prisms, for which it was found that the fly ash effectively suppressed expansion at cement replacement levels of 20% or more on an equal volume basis.

Stanton (184), Porter (196), and Pepper and Mather (187), in early studies of the use of fly ash to reduce expansion caused by alkali–silica reactions, noted that small additions of fly ash to mortars containing an opal aggregate may increase expansion, whereas larger amounts may result in reduced expansion. The general form of the relationship between ash quantity and expansion observed by these researchers is illustrated in Figure 7.16.

In a more recent study, Hobbs (197) reported that replacing 5% by weight of portland cement by four fly ashes, a ground slag or limestone fines had little effect upon the expansion of mortar bars tested at a critical alkali–silica ratio.

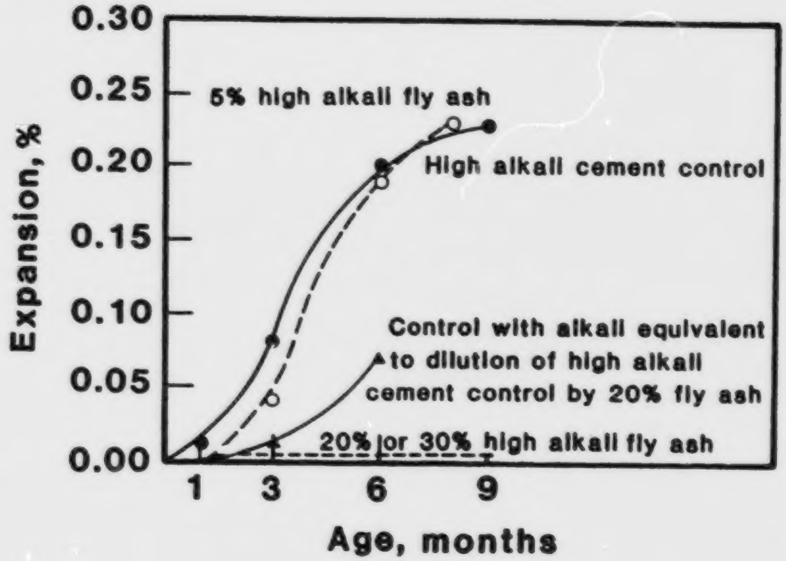

Fig. 7.15 — Expansion of concrete prisms containing high-alkali cement and fly ash with 30% flint/quartz aggregate (195)

Dunstan (191) has examined 17 fly ashes of both bituminous and sub-bituminous origin using Pyrex glass as aggregate. Among other conclusions, Dunstan suggested that the amount of fly ash corresponding to the pessimum point (the point of maximum expansion) was related to the CaO content. As CaO increased so the pessimum point increased with respect to fly ash replacement. This would lead to the conclusion that high-calcium fly ashes would show increased contribution to expansion at the levels of replacement normally used with low-calcium fly ashes and would only become effective in retarding expansion caused by alkali–silica reactions at higher replacement levels.

In summary, the following points may be made:

- There are substantial published data to show that low-calcium fly ashes are effective in reducing expansion caused by alkali–silica reactions when used at a replacement level in the range from 25 to 30%.
- The use of high-calcium ashes has received less attention and, hence, the background information relevant to their employment is less well developed. If they are to be used, there is some indication that effective replacement levels may

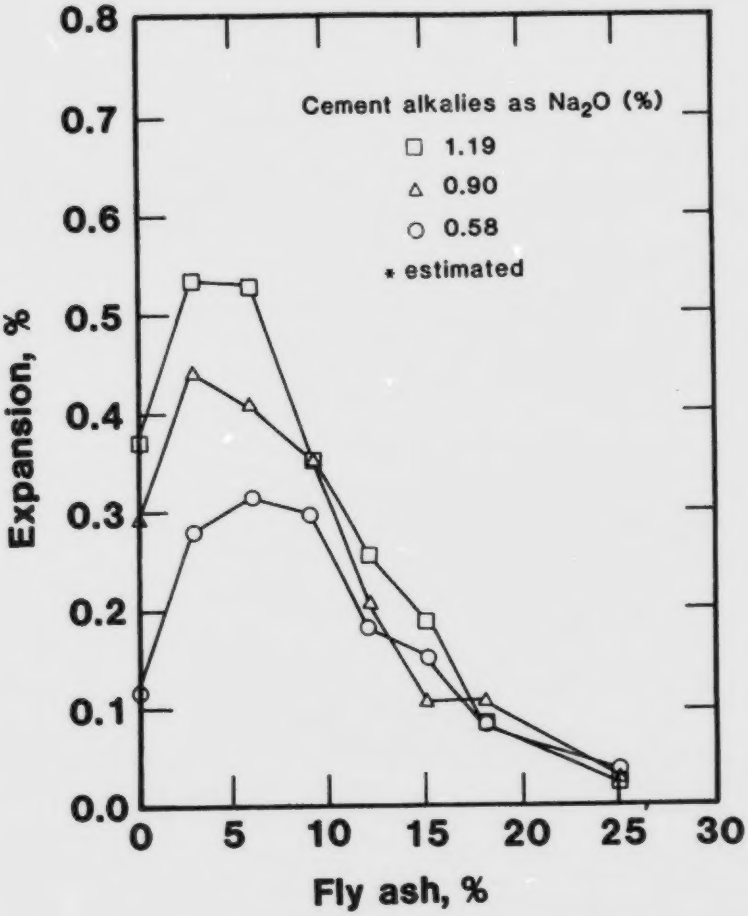

Fig. 7.16 — Effect of cement alkalis and fly ash on alkali–aggregate reaction (191)

be higher than for low-calcium ashes. Depending upon their ability to develop strength at early ages, concretes made with high fly ash replacement levels may or may not be acceptable.

— The mechanism and details of control of expansion caused by alkali–silica reactions are not fully understood, and there remains much research to be carried out before a satisfactory understanding can be developed.

Effects of Fly Ash on Corrosion of Reinforcing Steel in Concrete

Recently the corrosion of steel-reinforcing members has become an issue of concern with regard to the use of fly ash concrete in structures subject to corrosion caused by exposure to chloride ions from de-icing salts or sea water.

If the concrete cover over steel reinforcement is sufficiently thick and impermeable, it will normally provide adequate protection against corrosion. The protective effect is of both a physical and chemical nature in that the concrete functions in three ways:

- It provides an alkaline medium in the immediate vicinity of the steel surface.
- It offers a physical and chemical barrier to the ingress of moisture, oxygen, carbon dioxide, chlorides, and other aggressive agents.
- It provides a relatively electrically resistive medium around the steel members.

Under alkaline conditions (pH in excess of approximately 11.5), a protective oxide film will form at a steel surface that renders it *passive* against further corrosion.

During carbonation of concrete, if the depth of neutralization reaches the steel/concrete boundary, passivation may be reduced and corrosion may occur if sufficient oxygen and moisture can reach the metal surface. Chlorides or other ions may also destroy the protective action of passivation and encourage corrosion.

The Rilem Technical Committee on Corrosion of Steel in Concrete (198) made the following statements that serve to give perspective to this issue:

- "The efficacy of the (concrete) cover in preventing corrosion is dependent on many factors which collectively are referred to as its 'quality.' In this context, the 'quality' implies impermeability and a high reserve of alkalinity which satisfies both the physical needs and chemical requirements of the concrete cover. If the concrete is permeable to atmospheric gases or lean in cement, corrosion of the reinforcement can be anticipated and good protection is attempted by the use of dense aggregate and a well compacted mix with a reasonably low water-cement ratio.
- "If chloride corrosion is excepted, it is now usually agreed that carbonation of concrete cover is the essential condition for corrosion of reinforcement."

As was discussed in a previous part of this section, the issue of carbonation of fly ash concrete has received some attention in recent years. However, it is the authors' opinion that carbonation of fly ash concrete is not a matter of concern if attention is given to obtaining adequate impermeability in the concrete mass.

In 1950, the question was raised (199) as to whether there was a possibility of corrosion of reinforcing steel in fly ash concrete by the sulphur-containing components of fly ash. Gilliland (200) noted that most of the sulphur in fly ash is present as sulphate and, therefore, would have an effect similar to the sulphate components in portland cement. Further, he pointed out that corrosion of steel is greatly affected by pH — at the high pH prevailing in concrete, corrosion rates would be expected to be slow. Ryan (201) presented further information on the same point and drew the following conclusions:

— "Sulphur compounds in fly ash are usually so limited by specifications that they are not materially different in the concrete, whether fly ash is used or not. Moreover, the alkaline condition in the concrete is unfavourable to a sulphate attack on steel.

— "Carbon in fly ash would appear by theoretical considerations to be much more significant in concrete than is sulphur. The actual effect should be investigated. However, if it is kept under 3 per cent in the fly ash, its percentage in the concrete becomes so small that if it is well dispersed its effect on the electrical conductivity of the concrete, and therefore upon the corrosion of the steel, should be quite minor."

These conclusions seem to be generally acceptable in the light of reported research which has shown that fly ash concrete does not decrease the corrosion protection of steel reinforcing when compared with normal concrete (50,202,203). One recent study by Larson et al. (204,205) has found that corrosion protection is increased by the inclusion of fly ash in concrete.

In regard to the quality of concrete cover to steel and the points raised by the Rilem Technical Committee (see above), fly ash may influence both permeability and the alkalinity of the system.

The permeability of fly ash concrete and the related issue of carbonation have been discussed previously in this section. It is sufficient here to reiterate that properly proportioned fly ash concrete, subjected to adequate curing, should in general be less permeable at late ages than corresponding plain concrete. The danger of permeability lies in the exposure of fly ash concrete to aggressive agents before it is mature, either as a result of inadequate proportioning, incomplete curing, or poor fly ash quality.

With regard to alkalinity, it has been suggested that because the pozzolanic reaction consumes calcium hydroxide, as it progresses, this may cause a decrease in the pH of the pore water in fly ash cement paste. The pore solutions in hydrated cement are highly alkaline, which, as Diamond (206) has shown, results from the presence of sodium and potassium ions rather than from the presence of calcium hydroxide. In studies of two fly ash cement systems, Diamond showed (206) that the alkalinity is determined almost totally by dissolution of sodium and potassium salts from cement; at quite early ages, the concentration of calcium in solution is reduced to low levels. In the samples studied by Diamond, pore solution pH was reduced from 13.75 in a control system to about 13.55 in the presence of fly ash.

Effects of Fly Ash on Concrete Exposed to Sea Water

The deterioration of concrete in marine environments is a complex subject and cannot be treated adequately in a review such as this. This discussion has been limited to an examination of some of the aspects of using fly ash in marine concrete, with regard to the rather limited amount of directly applicable published data, and some extrapolations from the many reports that have been published on the behaviour of plain concrete in the sea.

Exposure of concrete to the marine environment subjects it to an array of severely aggressive factors, including most of those discussed in the preceding parts of this section.

Concrete in the tidal zone, subjected as it is to alternating wetting and drying; wave action; abrasion by sand and debris; frequent cycles of freezing and thawing; corrosion of reinforcement; all occurring in a chemically aggressive medium, is the most severely attacked. Permanently immersed concrete is less severely affected (207,208).

Little direct observation of fly ash concrete in sea water has been reported in the literature, although research in this regard is in progress (209). Because of the present lack of information, it is perhaps permissible to speculate, on the basis of the previously considered effects of fly ash on concrete durability and in an effort to obtain some guidance, as to the likely consequence of using fly ash in marine concrete.

Concrete in the sea is subjected to the aggressive influences discussed above. In Table 7.8 these have been compiled to give a profile of the ways in which fly ash concrete might be affected by exposure to sea water.

Table 7.8 — Potential influence on fly ash concretes of aggressive agents contained in sea water

Form of attack	Influence of fly ash	Notes
Wetting/drying	None	If proportioning and curing adequate.
Freezing/thawing	None	If proportioning, air-entrainment and curing adequate.
Sulphate	Improved by low-calcium ash.	
Alkali–aggregate	Acts to reduce expansion.	
Corrosion of steel	None	If porportioning and curing adequate.
Permeability	Improved at late ages.	If proportioning and curing adequate.
Magnesium salts	Not known.	

Whereas it is considered that permeability is the major factor affecting the durability of concrete in sea water (208), it is evident from the above that fly ash has the potential to contribute to a number of aspects of concrete durability in the marine environment. It is clear also that this is an aspect of fly ash concrete behaviour that is greatly in need of research.

8. STANDARDS AND SPECIFICATIONS FOR THE USE OF FLY ASH IN CONCRETE

A number of countries have published national standards and specifications regulating the use of fly ash in concrete. In some cases, these have been adapted from standards developed to control the use of natural or calcined pozzolans, while in others, new standards specifically directed to fly ash or other supplementary cementing materials have been established. Recent comparative reviews of national standards have been published by Manz (210) and Rossouw and Kruger (211). Table 8.1 presents a compilation of the designations of the relevant national standards and specifications from nine countries. A summary of the main technical features of these standards is given in Tables 8.2 to 8.4.

The development of standards is an ongoing process that largely comprises the establishment of a consensus among different interests. It is a difficult task because materials such as fly ash frequently come into use long before their properties and qualities are fully understood. In addition, because there is little international trade in fly ash, there has been no need for consistency to be established between the national standards of different countries. Unfortunately, this has also resulted in a lack of consistency in terminology (212-219).

In general, the term *fly ash* appears to be accepted in English-speaking countries other than Britain where *pulverized fuel ash* (abbreviated to PFA) is employed. In French, *cendres volantes*, in German, *flugashe*, and in Spanish, *cenizas volantes*, are commonly used terms.

Until recently, fly ash was regarded as a pozzolan. However, as high-calcium fly ashes have become more widely used, it has been realized that not all of them require an external source of lime to produce cementitious properties, and, hence, are not strictly pozzolans. Manz (210) and others have suggested that the high-calcium fly ashes (the so-called Class C ashes) are best distinguished from the low-calcium (Class F) ashes by their cementing properties. Thus, a general term *mineral admixtures* has been suggested to describe all classes of slags, ashes, pozzolans, and other cement supplements, with a further distinction being drawn on the basis of their self-cementing capabilities. This form of classification has been proposed as being preferable to the current division of fly ashes into two classes, according to the rank of coal from which they originate, that is practised currently in Canadian (5) and U.S. (6) standards.

Table 8.1 — Designations of national standard specifications for fly ash for use in concrete*

Country	Designation of standard	Year	Reference**
Australia	A.S. 1129	1971	(212)
Austria	Onorm B3320		(213)
Canada	CAN3-A23.5-M82	1982	(5)
India	I.S. 1344-1968	1968	(214)
Japan	JIS A 6201	1967	(215)
Korea	K.S. L5405		(216)
U.K.	B.S. 3892, Parts 1 & 2 Revisions	1963 1982	(217)
USA	ASTM C 618-83	1983	(6)
USSR	GOST. 6269-63	1963	(218)

*From references 210, 211.

**Citations are to the most recently published revisions known to the authors.

Table 8.2 — Chemical requirements for fly ash for use in concrete*

			Canada class		Britain						USA class		
	Australia	Austria	F	C	B.S. 3892	Draft	India	Japan	Korea	Turkey	F	C	USSR
Free water (% max)	1.5	1.0	3.0	3.0	1.5	0.5		1.0	3.0	3.0	3.0	3.0	
LOI (% max)	8.0	5.0	12.0	6.0	7.0	7.0	12.0	5.0	12.0	10.0	12.0	6.0	10.0
MgO (% max)		5.0			4.0	4.0			5.0	5.0	5.0	5.0	
Sulphate (as % SO_3 max)	2.5		5.0	5.0	2.5	2.5	3.0		5.0	5.0	5.0	5.0	3.0
Total sulphur (as % SO_3 max)		3.5											
SiO_2 (% max)		42-60						45				40	
Al_2O_3 (% max)		16-32											
Fe_2O_3 (% max)		3-12											
Minimum S + A + F**							70		70	70	70	50	
CaO (% max)		5-20								6.0			
Free CaO (% max)		2.0											
Total alkalies (as % Na_2O max)									1.5				
Available alkalies (as % Na_2O max)							1.5				1.5	1.5	
Carbon (% max)		3.0											
Chloride (% max)		0.1											

*From references 210, 211.

**Sum of % SiO_2 + % Al_2O_3 + % Fe_2O_3.

Table 8.3 — Physical requirements for fly ash for use in concrete*

			Canada class		Britain						USA class	
	Australia	Austria	F	C	B.S. 3892	Draft	India	Japan	Korea	Turkey	F	C
Specific surface (Blaine, min. cm^2/g)		4-5000					2800	2400				
Sieve (max %; μm)**	10;150		34;45			12.4;45				0.3;200 8;87		34;45
Av. particle diam. (μm)									9			
Specific gravity (min)								1.95				

*From references 210, 211.

**Sieve requirements are expressed as the maximum permitted quantity of material (as a percentage) retained on a screen of specified aperture (expressed in μm units); e.g., a maximum permitted quantity of 34% retained at 45 μm is expressed as 34;45.

Table 8.4 — Performance requirements for fly ash for use in concrete*

		Canada Class		Britain						USA Class	
	Austria	F	C	B.S. 3892	Draft	India	Japan	Korea	Turkey	F	C
POZZOLANIC INDEX:											
With cement (min % of control, 28 days)	80	75					60/70	85	70	75	75
With cement (min % of control, 7 days)		68									
Lime (min MPa)						3.9		5.5		5.5	5.5
Sand Replacement									100		
Water requirement (max % of control)					95			102	105	105	105
SOUNDNESS:											
Autoclave expansion (max %)		0.8				0.8		0.5		0.8	0.8
Other tests	pat								10**		
Drying shrinkage (max % at 28 days)						0.1					
Drying shrinkage (increase over control %)		.03						.03		.03	.03
Alkali reactivity (max % expansion at 14 d)								.02		.02	.02
Alkali reactivity (max % redn. of expansion)		60									

*From references 210, 211.
**Le Chatelier expansion test.

Use of the term *mineral admixtures* has been criticized in the past as reflecting that use of these materials might be relegated to small quantities of *addition*, as is normally the case for chemical admixtures.

In Canada, the term *supplementary cementing materials* has been adopted in specifications (5). Although somewhat long, it has the virtue of describing precisely the role of these materials in most concretes.

Nature of Specifications for Fly Ash in Concrete

In general, there are two issues to be considered when examining specifications for materials such as fly ash:

- the degree to which the selection of properties regulated by the specification serves to protect the user from incorrect or inappropriate use of the product;
- the degree to which the test methods proposed for examination of these properties are suitable to the evaluation of the materials and are adequate to detect and exclude unsuitable materials.

On examining the national standards from many sources, it is clear that there is general (though not always well-substantiated) agreement that the following properties should be considered when assessing the suitability of fly ash for use in concrete:

- pozzolanic activity
- particle size or surface area
- carbon content or loss on ignition
- moisture content
- various chemical parameters.

For simplicity in specification documents, these qualities are frequently divided between chemical and physical requirements. Because some of the so-called physical requirements relate to the chemical activity of fly ash, a more appropriate distinction might be drawn between chemical requirements, physical properties, and performance requirements, and this approach has been adopted in this section.

Chemical requirements

Many national standards reflect the concern that components harmful to the properties or durability of concrete should not be introduced with fly ash. Some go further, and attempt to relate the performance of fly ash as a pozzolan to chemical composition. The following chemical requirements are frequently specified.

Moisture content: With the exception of India and the USSR, standards from most countries place limits on moisture content. This reflects largely a need to protect the purchaser from receiving ash in a wet state.

Loss on ignition is specified in all national standards, with the intention of limiting carbon content, the presence of which has been associated with difficulties in control of air-entrainment in fresh concrete (see Section 3). Loss on ignition is not a reliable parameter for this purpose because a number of other components in fly ash are volatile or decompose on heating.

Direct methods of determining carbon content are available using rapid tests and provide a more reliable measure of the presence of carbon in ash.

The distinction between loss on ignition (set at 5% max) and carbon (set at 3% max) is drawn explicitly in the Austrian national standard.

Sulphate: Most national standards limit the concentration of sulphate introduced into concrete with fly ash. This is done to prevent interference with the setting of cement and to reduce the possibility of expansive deterioration of the hardened concrete. Similar limitations are usually placed on other concrete components. There is no general agreement between national standards as to the level of sulphate permissible in fly ash.

Magnesium oxide: Although there is no evidence that magnesium in fly ash is present in the form of periclase (MgO), many standards reflect the same limitation on MgO content that is applied to portland cements.

Available alkalis: The concentration of alkalis in cementitious materials is frequently limited to prevent efflorescence and to control alkali–aggregate reactions. Excessive sodium or potassium content in fly ash may contribute to efflorescence in hardened concrete. Winer and Malhotra (220) have examined accelerated test methods for the determination of soluble alkalis, that are more readily applicable to high-calcium fly ashes than the currently specified tests.

Chloride: Only the Austrian specification for fly ash limits chloride (to a maximum of 0.1%) in fly ash. In view of the role of chloride in the corrosion of steel reinforcement, some investigation of the need to consider chlorides in fly ash may be required in North America.

Major oxides: Some standards require that the silica content of fly ash be in excess of a specified minimum value, whereas others require the sum of the alumina, silica, and iron oxide content to be in excess of a minimum value. It has been suggested (221) that the sum (SiO_2 + Al_2O_3 + Fe_2O_3) is related to the quantity of glassy particles in fly ash. There is no evidence that the content of these oxides is directly related to the performance of ash in concrete (91,93).

Physical properties

Except in the USSR, national standards for fly ash require control of fineness either through particle size or surface area. Although not generally specified, some form of mass–volume relationship is usually required as a part of the tests used to determine pozzolanic activity and may be required to establish uniformity of an ash source.

Particle size or surface area: There is general agreement that pozzolanic activity is affected by the particle size distribution or fineness of fly ash, and there is considerable evidence that the presence of coarse particles in ash is deleterious (see Sections 3 and 4). There is, however, disagreement about the method of testing and the limits to be placed on coarse particulate content from one standard to another.

In general terms, the particle size properties of a material such as fly ash may be measured by one of three types of test:

- — wet sieving
- — dry sieving
- — air permeability.

Australian, Canadian, British, U.S., and Turkish standards require the use of wet-sieving methods to determine the residue on one or more screens of specified mesh size.

The Turkish and the Australian standards both require the use of two screens. Other standards are restricted to determination of retention on a 45-μm screen.

The wet-screen techniques, although convenient in that they employ inexpensive equipment, may produce erroneous data with ashes containing substantial water-soluble materials or components that react with water. The use of wet sieving methods with high-calcium fly ashes should be considered in this regard.

A simple, but more expensive, technique that is not subject to the influences of water is the dry sieve method using the Alpine Air-Jet Sieve. Details of the method and its comparison with conventional methods for determination of fineness of cement were reported by Malhotra and Zoldners (222). A direct comparison of wet and dry screening of ten different fly ashes was made by Berry and Hemmings (223). It was found that correlation between fineness as determined by the Alpine Air-Jet Sieve and the wet screen (ASTM C430) was excellent, but that the wet screen consistently gave a value for the quantity retained at 45 μm in excess of that found for the dry method. In Canada, the Alpine Air-Jet method is currently used on a routine basis by Ontario Hydro for quality control of ash fineness.

A much less satisfactory approach to fineness control, still commonly used, is to specify *surface area* as determined by air permeability. This approach is less valuable for a number of reasons:

- Surface area is not a definable physical property for fine particles unless it is related to the method of measurement.
- Methods of determination based on air permeability, such as are used for portland cements, are not reproducible with most fly ashes.
- There is no clear relationship between surface area as determined by the more common methods and strength development in fly ash concretes.

Mass/Volume Relationships: For practical reasons, it is necessary to know the approximate volume occupied by a given mass of fly ash. Because most fly ashes contain hollow particles, none of the displacement methods used measures true particle density. The property determined is usually one form or another of apparent density.

Performance Requirements

Ideally, specifications for materials such as fly ash should be based upon measurements of performance. Unfortunately, those performance qualities that are most frequently required are among the most unreliable aspects of the specifications regulating fly ash use.

The most frequently specified requirements reflect attempts to determine the pozzolanic activity of fly ash and its effect on water demand, its potential for alkali reactivity, and its influence on soundness and shrinkage. Of these, alkali reactivity, soundness, and shrinkage determinations generally follow the approaches taken in corresponding specifications regulating the properties of cements.

Pozzolanic activity is the most difficult of the fly ash properties to define and to determine, largely because it is not understood. Pozzolanic activity comprises the reaction of an alumino-silicate with calcium hydroxide to form cementitious products; it is usually determined by one or more of the following classes of test;

- determination of the relative strength of fly ash and control mortars after curing for 28 days;
- determination of the relative strength of fly ash and control mortars after curing for seven days under accelerated conditions;
- determination of the strength of fly ash–lime mortars after curing for 27 days.

In general, it is agreed that these tests are an inadequate means to predict fly ash performance in concrete. Their inadequacy results principally from the fact that the strength of a cemented composite is not determined solely by the extent of the formation of cementitious components. Other factors are involved and generally cannot be accounted for in the normal test procedure.

If the present tests have any value, it may be as a means to detect gross variations in the reactivity of fly ash from a source that has been proven to be useful by direct tests in concrete mixes.

In summary, most of the standard specifications, though adequate for overall control of fly ash quality, continue to limit properties and require the use of tests that are now understood as largely irrelevant to the behaviour of ash in concrete. On the other hand, relevant properties are not always considered (for example the particle size of ash is ignored in the USSR standard) and relevant or best-suited tests are not always required (viz. the use of LOI rather than carbon determination).

Butler (224) has questioned the philosophical basis of the ASTM specification for fly ash in terms that may well be considered in relationship to other national standards.

In essence, he proposes that specified tests for ash should provide for three needs:

- ensuring that the ash will not be harmful to the desirable properties of concrete;
- indicating the potential performance of the ash in concrete;
- monitoring key properties to ensure uniformity.

The first two of these require that ash from a new source be exhaustively examined prior to its introduction into the concrete marketplace, and that regular quality-assurance tests be performed to ensure that ash from a given source remains suitable for use in concrete. Neither of these activities require that testing be performed on every delivered batch of ash.

The third need expresses the requirement for quality control and does demand some routine testing to be applied at the batch level.

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CHAPTER 3

CONDENSED SILICA FUME IN CONCRETE: A WORLD REVIEW

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1. INTRODUCTION

Condensed silica fume (CSF) is a by-product of the smelting process used to produce silicon metal and ferrosilicon alloys. Other names for CSF that can be found in the literature are; microsilica, ferrosilicon dust, arc-furnace silica, silica flue dust, amorphous silica, and volatized silica. Even "very fine grained siliceous fly ash" has been used as a definition for condensed silica fume. Besides CSF, microsilica seems to be the most commonly accepted name. Although no distinction is made here between the types and forms of CSF, all the CSF used in the investigations reviewed here comes from silicon metal, or ferrosilicon alloy production containing more than 75% silicon, and it is implied that all share the following main characteristics:

- SiO_2-contents from 85 to 98%;
- mean particle size in the range 0.1 to 0.2 μm;
- spherical shape with a number of primary agglomerates;
- amorphous structure.

CSF for use in concrete is either in a *natural* state, densified, or in slurry form mixed with 50% water by weight. General field experience as well as laboratory tests have shown remarkably little difference in the properties of hardened concrete containing CSF with different characteristics or in different forms. This experience is in sharp contrast to that with different fly ashes. However, the type and form of CSF may influence significantly the properties of fresh concrete; particularly the rheological properties. At present it is not possible to relate such differences to specific physical or chemical characteristics of the CSF.

This review* is intended to cover the properties of concrete containing CSF in the fresh state, during hardening, and in the hardened state, with emphasis on durability. It is based on published reports, of which about 400 are available, the majority of which are written in Norwegian. Most of the reports contain original laboratory data, some are review articles covering limited topics, and a few are concerned with laboratory investigations of concrete from old structures.

The first tests of CSF in concrete were made in the early 1950's at the Norwegian Institute of Technology. At the same time CSF was included among a large number of additive–cement combinations to produce concretes for long-term exposure to the acidic water of high sulphate content in a tunnel segment in the Oslo alum-shale region. Results of these tests were reported after 20 years of exposure, and, after 30 years, a final report is now in preparation.

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*Submitted, February 1986

The first documented use of CSF in structural concrete took place in 1971 at the Fiskaa smelting plant in Norway, and the concrete has since been investigated on several occasions. Since the start of large-scale filtering in the mid-1970's, the use of CSF, both in practice and in laboratory investigation, started in several places. In Gothenburg, Sweden, a ready-mixed concrete plant used CSF extensively, including in concrete for a large wharf. In Denmark and Norway ready-mixed concrete plants also began production, and systematic laboratory work started at the Norwegian Institute of Technology. In Iceland, investigations with a view to reducing the effects of alkali–aggregate reactions using CSF were commenced resulting in the production of a cement containing 7.5% CSF.

Outside Scandinavia, reports began to appear at the end of the 1970's, particularly from Canada, where practical use of CSF in ready-mixed concrete was started in 1981. Since then, research work and practical use of CSF in concrete has begun in many countries, and is spreading rapidly.

When the properties of CSF concrete are considered, it is important to keep in mind that CSF is used in two different ways:

- As a cement *replacement*, to obtain reduction in the cement content — usually for economic reasons.
- As an *addition* to improve concrete properties — both in fresh and hardened state.

For normal, low-grade structural concrete the required strength can be obtained with an extremely low content level of cement when CSF is used. The debate in Scandinavia regarding CSF in concrete has been focused mainly on the durability aspects of this approach. The true promise of CSF, however, lies in the approach aiming to design concrete for specific production processes and to achieve better durability, or to enable the production of high-strength concrete on a routine basis.

Norwegian Standards allow up to 10% content of CSF by weight of cement in concrete. Normal usage is generally less than this. The term CSF concrete as used in this review refers to contents of 10% CSF or less, unless otherwise specified. High CSF content combined with superplasticizers and extremely low ratio of water to cement (W/C) are the basis for a new type of concrete with special properties which is not discussed here.

In this review the W/C is calculated on the basis of cement content only. The water to cement + silica fume (W/C+S) is used for CSF mixes, where S stands for the amount of CSF. CSF content is given as a percentage of weight of cement.

2. POZZOLAN AND FILLER EFFECTS

CSF is both a reactive pozzolan and a very effective filler. Both these properties combine to explain the effects of CSF on the properties of cement-based products.

Reactivity and Reaction Products

A number of reports have been published on the pozzolanic reactivity of CSF. Three articles by Hjorth (1) and Regourd (2,3) review the subject.

The pozzolanic reactivity of CSF in cement pastes has been demonstrated by measuring the amount of calcium hydroxide at different times in pastes with varying contents of CSF. Thermal gravimetric analysis – differential thermal analysis (TGA-DTA) and X-ray diffraction methods have been used. The results generally show high pozzolanic reactivity: Regourd et al. (4,5), Sellevold et al. (6) and Cheng-yi and Feldman (7,8). Traetteberg (9) found medium reactivity, whereas Scheetz et al. (10) and Chatterji et al. (11) concluded that the reactivity was low. Other studies on pozzolanic reactivity include Traetteberg (12) and Chatterji et al. (13). Figure 2.1 shows calcium hydroxide contents for various CSF contents determined for mature cement-paste specimens. Extrapolation of the curve indicates that roughly 24% CSF will eliminate

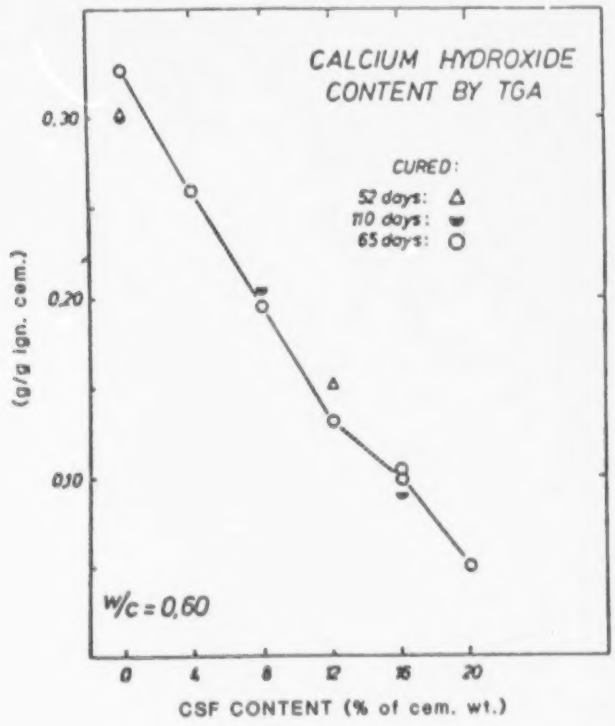

Fig. 2.1 — Calcium hydroxide contents of mature pastes made with white portland cement, with water-to-cement ratio 0.60 and various amounts of CSF (6).

the calcium hydroxide. This number varies in the literature, and depends both on the method used to determine the calcium hydroxide content and on the composition of the cement.

CSF has been found to have an accelerating effect on the hydration of white portland cement (6); this effect is roughly equal to the effect of a very fine calcium carbonate filler. Figure 2.2 shows the calcium hydroxide contents versus time for a reference paste as well as for one containing 12% CSF. Up to about two days the CSF mixture has a higher calcium hydroxide content than the reference mixture, but then the curves cross, presumably because calcium hydroxide is consumed faster by the pozzolanic reaction than it is generated by the cement hydration.

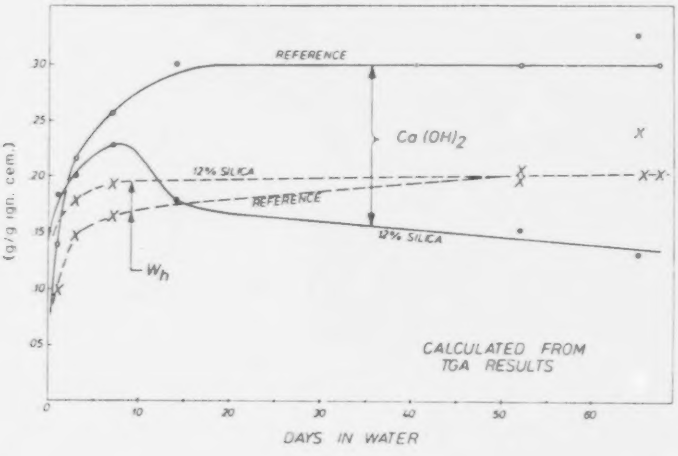

Fig. 2.2 — Non-evaporable water content (W_n) and calcium hydroxide content for white portland cement pastes (W/C = 0.60) with and without 12% CSF (6).

Wu and Young (14) studied the reaction of CSF with tricalcium silicate (C_3S) and with calcium hydroxide. They concluded that CSF accelerates the hydration of C_3S. Halse et al. (15) found that C_3S hydration was enhanced rather than accelerated by CSF, whereas Traetteberg (12) concluded that when lignosulphonates were used, it led to a marked reduction in the cement hydration over long periods, both with and without CSF. The data in reference 12 have been re-evaluated by Markestad (16).

Cheng-yi and Feldman (7) studied the hydration of cement paste and mortar with varying amounts of CSF and ground quartz sand. Both additives were found to accelerate the cement hydration at early ages, but after 14 days the calcium hydroxide content was eliminated in pastes containing 30% CSF. Mixtures with 10% CSF led to a reduction in the calcium hydroxide content of about 8% by weight of cement, implying a calcium to silica ratio (C/S) of about 0.7 — a very low value. For mortar mixtures (8), a similar calculation yields a C/S value of about 1, which value corresponds closer with other observations.

The pozzolanic reactivity has been investigated in mixtures containing only CSF and calcium hydroxide. Buck and Burkes (17) detected well-crystallized calcium silicate hydrate (CSH I) after seven days of curing at 38°C. Grutzeck et al. (18,19) observed a silica-rich gel on CSF surface shortly after having mixed CSF in calcium hydroxide solution or in cement paste. The gel later combined with calcium hydroxide to form CSH.

Wu and Young (14) found that CSF behaved similarly to synthetic silica fume, differing only in rates of reaction according to their specific surface areas. According to Wu and Young three kinds of CSH are formed in C_3S–CSF systems:

- — that formed directly from C_3S hydration;
- — that formed from the reaction between calcium hydroxide and CSF (with a slightly lower C/S);
- — that formed by reaction between CSH and CSF (with a very low C/S and high degree of polymerization).

The latter will form only in mixtures containing more CSF than needed to consume all calcium hydroxide, i.e., it is not relevant for normal CSF concrete.

Kurbus et al. (20) mixed CSF with calcium hydroxide at water-to-solid ratio of 0.50, and cured the pastes at 55°C and 90°C. The reaction was temperature dependent; at 90°C, 68–95% of added lime had reacted after 2.5 hours (depending on initial quantities), whereas at 55°C only 25–55% had reacted in 2.5 hours. At 20°C the reaction has been found to be very slow for a mixture with a C/S of 1.0 (6), but after 110 days of reaction there was no sign of calcium hydroxide on the TGA curves.

The C/S in the range of 0.9 to 1.3 have been reported for cement–CSF mixtures (4, 5, 6, 9). Regourd (2) found the C/S to decrease with increasing content of CSF, a natural result because a high CSF content implies a higher fraction of CSH formed by the pozzolanic reaction in the total amount of CSH.

A consequence of the low C/S in the CSH is an increased capacity to incorporate foreign ions, such as alkalis and aluminium. The high capacity to incorporate alkalis has been demonstrated by analysis of pore-water squeezed out of hardened cement–CSF pastes as shown by Diamond (21), and Page and Vennesland (22). These factors can partly explain the resistance of CSF concrete to aggressive chemicals and alkali–aggregate reaction expansions (5).

The microstructure of the binder phase in CSF concrete appears very dense and amorphous (2). Diamond (23) reports that in contrast to normal concrete, in a properly formulated CSF concrete, the CSH gel particles cannot be "visualized as individual particles, but rather as a massive, dense structure." Calcium hydroxide appears as small local crystals, rather than large masses which act as flaws in normal pastes. According to Diamond (23) and Regourd (3), the dense paste structure essentially extends to the true aggregate boundary in a dense CSF concrete. This structure eliminates the normal porous region of about 40–50 μm, rich in calcium hydroxide, which surrounds aggregate grains in normal concrete. These observations apply for high CSF content pastes in high-strength mixtures. In CSF concrete of normal strength with moderate CSF content, the changes in microstructure are less marked.

The amount of water bound in the CSH formed by the pozzolanic reaction was found to be the same as that contained in the calcium hydroxide (6). The analysis of the data by Meland (24) shows no increase in the bound water per gram of cement in the pastes containing CSF, which is in agreement with the data in reference 6. Diamond (21), however, found the bound water content to increase per gram of cement in CSF cement pastes compared to pure cement pastes. Cheng-yi and Feldman (7) found that, for a ratio for W:C + S of 0.45, the non-evaporable water per gram of cement was 0.207 for a reference paste, 0.172 with 10% CSF, and 0.219 with 30% CSF. For a ratio for W:C + S of 0.25 the numbers were: 0.144 in a reference paste, 0.138 with 10% CSF, and 0.163 with 30% CSF. Thus, the picture is not entirely clear at present. It is consistently observed, however, by calorimetry and by the development of non-evaporable water content, or calcium hydroxide over time, that CSF accelerates the hydration of cement.

In a series of paste mixtures where different amounts of CSF were added at a constant ratio of water to cement, it was found that the total volume porosity to water in the pastes was independent of the CSF content (6). This result implies that the chemical shrinkage caused by the pozzolanic reaction is greater than that of the cement hydration; it was estimated to be 12 cm^3/100 g CSF, compared to a value of about 5 cm^3/100 g cement. As a consequence of this, CSF concrete cured without access to water will experience a higher degree of self-desiccation and, consequently, a lower internal relative water vapor pressure. This has been confirmed by measurements carried out by Nilsson (25), where a mixture with a ratio for water to cement of 0.40 and 10% CSF had an internal RH value of 70% after six months of sealed curing.

Pore Structure

Pore structure plays a major role in determining the permeability and, thereby, durability properties of cement-based products. Recent work by Mehta (26) and Manmohan and Mehta (27) have demonstrated a relationship between pore structure, permeability, and durability for blended cements. The pore structure of cement–CSF pastes has been studied by Sellevold et al. (6) using water adsorption, mercury penetration, and low-temperature calorimetry. They concluded that increasing CSF content at constant ratio of water to cement did not change the total porosity as measured by water adsorption, but rather led to a refinement of the pore structure, i.e., less of the pore space consisted of capillary pores, where water can freeze and mercury can penetrate. For pastes in which part of the cement was replaced by CSF on a 3:1 basis and the water content was kept constant, the capillary porosity was unchanged, indicating that CSF was roughly three times as "efficient" as cement in reducing capillary porosity. By comparing pore structure data for CSF pastes to pastes where an almost inert filler of equal fineness was used, it was concluded that most of the pore-refinement effect was caused by the pozzolanic activity of the CSF. Figure 2.3 shows mercury penetration results for mature pastes.

Traetteberg (28) measured mercury penetration in mortars with varying CSF contents, and concluded that CSF was very efficient in subdividing the pore space.

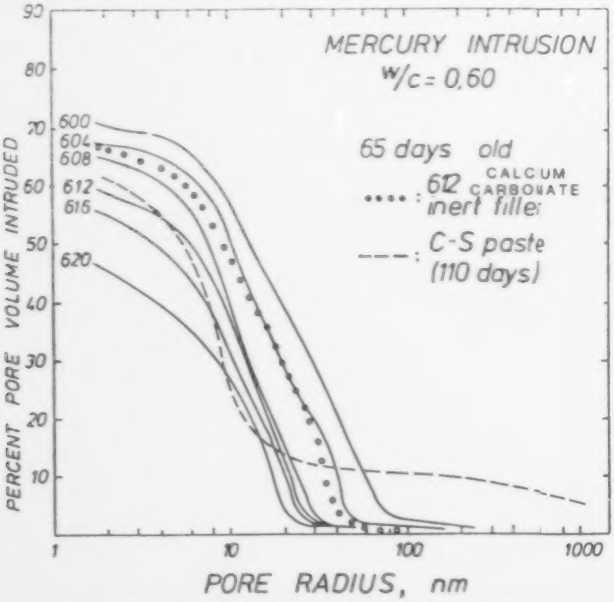

Fig. 2.3 — Mercury intrusion in mature white portland cement pastes. The two last digits in the identification numbers indicate the % CSF added. The inert filler is a very fine, precipitated calcium carbonate. The C-S paste is a calcium hydroxide–CSF mix with C/S = 1.0, (6).

Mehta and Gjørv (29) measured mercury penetration in cement pastes with a water-to-cement ratio of 0.74 and in equivalent pastes where 30% of the cement volume was replaced by fly ash, CSF, or an equal volume of the two. The results showed that at 90 days the total penetration was equal for the control and for the CSF pastes. For the control paste, however, more than 50% of the available pore space was large pores (>0.1 μm) whereas the CSF paste contained only about 10% large pores. Fly ash also had a pore-refinement effect but far less than CSF.

Cheng-yi and Feldman (8, 30, 31) studied the porosity of pastes and equivalent mortars with 0, 10, and 30% CSF as replacement for cement in a 1:1 ratio. For pastes the results of mercury intrusion agreed with others; increased CSF dosage leads to a finer pore structure. After the first intrusion, the mercury was evaporated and a second intrusion was performed. Hysteresis between the two curves indicate discontinuity in the pore structure. The pore structure may be "broken up" during the first intrusion. This hysteresis increased markedly with increasing CSF content. For mortars (31) the effect is even more pronounced. Figure 2.4 illustrates these effects with data from (30) and (31).

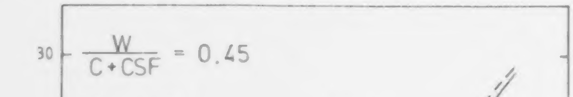

Fig. 2.4 — Mercury intrusion and reintrusion into 90-day-old cement pastes and mortars (plotted from data in Feldman and Cheng-yi, 30,31).

The authors relate this effect to the reaction of CSF with calcium hydroxide, particularly the high concentrations of calcium hydroxide around sand grains in mortars. They demonstrate that CSF mixtures have higher ratios between mortar and paste compressive strength than mixtures without CSF, and they attribute this to the improved bond between sand and binder matrix. They have also observed that CSF mortars have a higher fraction of pores with diameters above 100 nm relative to equivalent pastes than is the case for mortars and pastes without CSF. That a pozzolanic reaction between CSF and calcium hydroxide at the interface improves the bond appears to be natural, but we find it less natural that such an improved bond phase has a coarser and more unstable pore structure than is found in mixtures with no CSF.

The Technological Institute in Denmark has developed a method to estimate the capillary porosity of concrete by microscopic examination of thin sections impregnated with fluorescent epoxy. Applying this method to CSF concretes from field and laboratory, Christensen (32) concluded that, in terms of reducing capillary porosity of concrete, CSF has an efficiency about three times that of cement.

Conclusions: Pozzolan and Filler Effects

CSF is considered to be a very reactive pozzolan. When used in cement systems it produces a CSH gel with a lower C/S than the cement hydration, and, consequently, it has a high capacity to incorporate foreign ions, particularly alkalis. The nature of the hydration products of CSF, and its influence on cement hydration, are not entirely understood at present. CSF also has a definite filler effect that is believed to distribute the hydration products in a more homogenous fashion in the available space.

These two factors have the combined effect to refine the pore structure when CSF is added to cement-based mixtures. The refinement of the pore structure leads to reduced permeability, and is considered to be the main factor responsible for the influence CSF has on mechanical and durability properties of concrete.

3. FRESH CONCRETE

The influence of CSF on the workability of concrete depends somewhat on the type of concrete. Generally, the addition of CSF to a given mixture will lead to a lower slump, and to a more cohesive mix. The "static" and "dynamic" behavior of CSF concrete do not relate in the same way as for normal concrete, i.e., the slump measure does not predict the response to vibration in the usual way. For practical purposes it is generally recommended that the slump should be 20 to 30 mm higher for a CSF concrete to obtain the same workability as that for normal concrete, which should be kept in mind when considering water-demand tests based on equal slumps.

Water Demand

Systematic measurements of water demand to reach a given slump for different CSF contents have been made by Johansen (33) and Løland and Hustad (34). For very lean concrete (cement 100 kg/m^3) it was found that the water demand decreased as CSF was added (34), as has been reported by Aitcin et al. (35) for lean mixes with less than 10% CSF.

In concrete with a cement content of more than 250 kg/m^3, the water demand will increase when adding CSF, or even 1:1 replacement of cement by CSF, when no water-reducing agents are used. Sellevold and Radjy (36) analysed the data from references 33 and 34 together with the data by Dagestad (37) on the water demand in concrete mixed with three types of cement, different contents of water-reducing agents, and 0, 8, and 16% CSF by weight of cement. They found that the increased water demand per kilogram of CSF added was in the order of one litre. However, water-reducing agents had much more pronounced effect on the CSF concrete. A lignosulphonate content (dry) of 0.2 to 0.4% by weight of cement was sufficient to equal the water demand of the control mixes and those with 10% CSF (Figs. 3.1 and 3.2). It was also found

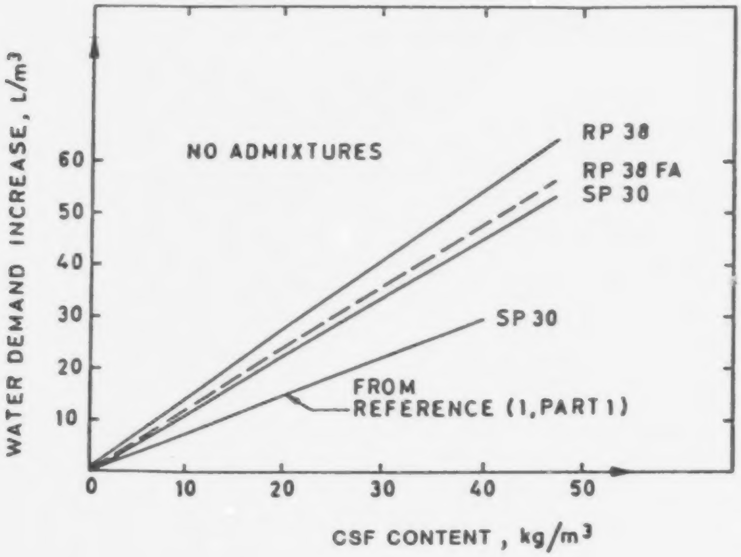

Fig. 3.1 — The influence of CSF content on the water demand of concretes without water-reducing admixtures (36).

***Key:** SP 30 = Ordinary portland cement*

RP 38 = Rapid-hardening portland cement

RP 38FA = RP 38 with 20% fly ash.

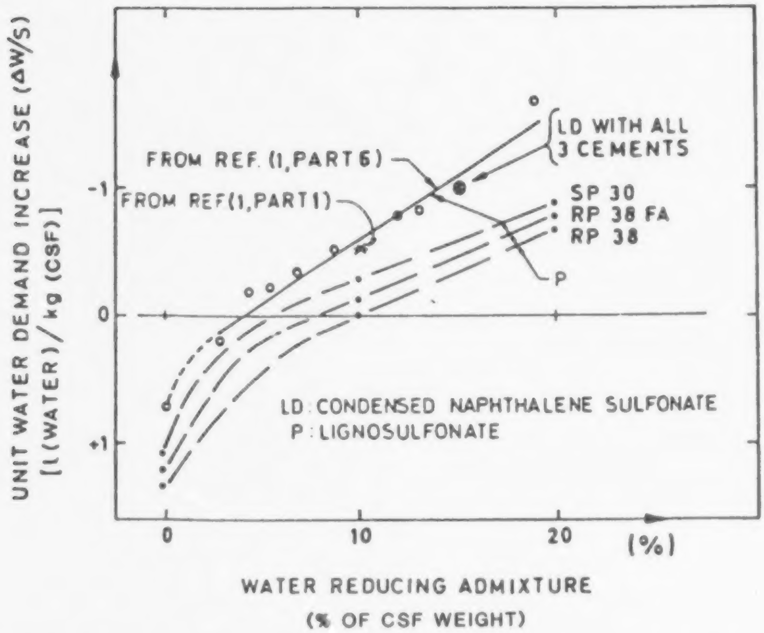

Fig. 3.2 — The influence of water-reducing admixture dosage on the water demand of CSF concrete (36).
Key: SP 30 = Ordinary portland cement
RP 38 = Rapid-hardening portland cement
RP 38FA = RP 38 with 20% fly ash.

that the amount of water-reducing agent should be calculated by weight of CSF to keep the water demand near that of the control concrete. A content of 4% dry lignosulphonate by weight of CSF is a good starting point for CSF contents between 5 and 15% by weight of cement, according to the Norwegian experiences. The investigations cited here, as well as general Norwegian experience show that lignosulphonate-based water-reducing agents are as or more efficient in reducing water demand in CSF concrete than are superplasticizers.

Markestad (38) also analysed the data from Dagestad (37). He concluded that the water reduction achieved by water-reducing admixtures in CSF concrete was directly proportional to the admixture concentration in the mixing water, rather than to the amount of CSF. He proposed a mixture-proportioning method based on an efficiency factor of a given admixture.

Maage and Dahl (39) measured water demand for concretes with different types of cement and various CSF contents. At a constant content of lignosulphate the water demand increased with increasing CSF content for all types of cement.

Carette and Malhotra (40) and Petersson et al. (41) have also measured water demand in CSF concrete. Their conclusions are in general agreement with the previous discussion, but are not numerically identical. As already mentioned, the type of CSF and its specific interaction with all the materials in a given concrete determine the water demand of concrete. Systematic laboratory tests based on fixed mix proportions in a control concrete have little value. When CSF is used, the chosen mixture proportioning may not be the optimum. For instance, the great fineness of CSF usually permits a coarser grading curve for the other constituent materials.

Adsorption of water-reducing admixtures on CSF has been measured by Meland (42) and by Buil et al. (43).

Concrete Colour

CSF may vary considerably in colour which in turn affects the colour of the fresh concrete. Generally, CSF darkens the concrete. Bellander (44) determined the *degree of darkness* of concretes made with a light and a dark CSF according to a Swedish Standard. The dark CSF produced a darker fresh concrete, but after 20 days of storage in laboratory air there was no measureable difference between the two CSF concretes and the control concrete. The initial difference is presumably eliminated by drying-carbonation effects.

Cohesiveness — Stability

Increased cohesiveness is the most obvious difference between the CSF concrete and normal concrete. One consequence of this cohesiveness is reflected in dynamic workability tests such as *Thaulow strokes* (a Norwegian test somewhat analogous to the ASTM flow table test) or a modified Vebe test. Both Johansen (33) and Maage and Dahl (39) found that, at equal slumps, concrete containing CSF required more energy input for a given flow. In practice, this problem is overcome by maintaining higher slump for CSF concrete. The cohesiveness imparts stability to the mix, an effect of major importance in connection with flowing concretes.

To produce high-quality concrete for a fertilizer storage silo, a mixture was proportioned using about 15% CSF and a high content of a superplasticizer. Helland (45) reports that the trial mixtures were extremely sticky and hard to handle. The Tattersall Two-Point Workability Apparatus was used to test the mixtures, and the problem was solved by entraining about 8% air in the concrete. This clearly demonstrated that the slump measure is not useful to characterize such extreme mixtures.

Stability of concrete is commonly characterized in terms of bleeding. Quantitative measurements of bleeding are rare, but in two such studies Johansen (33) and Maage and Dahl (39) found that CSF used as a cement replacement led to a large reduction in bleeding, even for mixtures with no water-reducing agents and, therefore, increased water contents. Bellander (44) states in a review article on practical experience in Sweden that CSF also improves the ability of concrete to be handled and transported without separation. In a comprehensive study of 25 concrete mixtures (34), the bleeding and separation tendencies were evaluated qualitatively. Again the conclusion was that CSF greatly improved the stability of concrete, particularly in very lean mixtures.

Plastic Shrinkage

Plastic shrinkage and cracking takes place when evaporation from a fresh concrete surface exceeds the rate of bleeding water from the concrete. The fact that bleeding can be practically eliminated in CSF concrete makes it vulnerable as regards to cracking. Johansen (46) made a systematic investigation of plastic shrinkage cracking, and concluded that the critical time was just at about the time when the setting of the concrete took place. The above problem can be eliminated by applying a proper curing procedure to the concrete surface. Practical experience shows that under conditions of fast evaporation (wind and sun), curing measures must be taken immediately after placing the concrete.

Setting Time

The setting characteristics of cements are measured on pastes with a standardized consistency, using a Vicat apparatus. Maage (47) measured setting times for cement pastes with 0 and 10% CSF. All pastes, except the control paste, were mixed with 0.4% dry lignosulphonate by weight of cement. The setting of all the pastes with the admixture were retarded relative to the control. However, the retardation effect of the lignosulphonate was much less in pastes containing CSF than in pure cement paste. This observation agrees with the practical experience that CSF concrete can tolerate a higher lignosulphonate content than normal concrete without suffering from unacceptable retardation. Isothermal calorimetry data on pastes with and without CSF and lignosulphonates (48) are in agreement with this.

Penetration measurement on mortars is a more relevant test than the Vicat test. Bellander (44) found a tendency to longer setting time with increased CSF content for concretes of equal strength, whereas Petersson et al. (41) found CSF content had little influence in concretes with constant cement plus CSF content. Neither of these investigations used water-reducing admixtures, and they are, therefore, of little relevance because almost all CSF concrete is produced with water-reducing agents.

Considerable practical experience exists concerning the setting time of CSF concretes with admixtures, but no comprehensive laboratory investigations have been reported. As for CSF and control concretes of equal 28-day strength, the former will normally have a longer setting time and slower early strength development, because it has a higher W:C + S ratio.

A commonly used method for practical control of the setting time and early strength development is to use a combination of lignosulphonate and superplasticizer; and to vary the relative contents to achieve the desired results.

Conclusions: Fresh Concrete

The major effects of CSF on the workability of concrete are to increase its cohesiveness and stability. Consequently, bleeding is greatly reduced. The increased cohesiveness means that a higher slump is needed to match the workability of a control concrete. The CSF addition leads to an increased water demand. Water-reducing admixtures or superplasticizers are necessary to realize the potential of CSF in practice. The use of such admixtures has a greater effect in CSF concrete than in control concrete.

The lack of bleeding in CSF concrete makes it more vulnerable to plastic shrinkage cracking than ordinary concrete. Protective measures must be taken under conditions of high evaporation rates from the concrete surface.

4. HARDENED CONCRETE — STRENGTH DEVELOPMENT

Temperature Effects

A large number of investigations have reported strength development with respect to time for CSF concretes. Most of these are confined to compressive strength and curing at 20°C. In some reports heat curing has been used. In this section only compressive strength development and temperature effects are considered for moist-cured concrete.

For moist-curing at about 20°C, it is established that the strength development for a CSF concrete is slower than for a control concrete of equal 28-day compressive strength. This difference increases with increasing CSF content and decreasing temperature. It does not mean, however, that high early strengths cannot be obtained using CSF. One-day strength as high as 100 MPa has been reported by Bürge (49) for a concrete quality that can hardly be made with portland cement alone. High early strength in CSF concrete without the use of heat-curing or accelerators also means high later-age strengths. The percentage of the 28-day strength that is obtained the first day increases with a decreasing water-to-cement ratio for normal concrete. The percentage for CSF concrete appears to be the same as for normal concrete with the same water-to-cement ratio but of course the CSF concrete characterized this way has a higher absolute strength at 28 days.

CSF contributes most to strength development at 20°C in the time range from 3 to 28 days. Empirical relationships between short time and 28-day strengths are, therefore, not applicable to CSF concrete, which has a much higher strength gain than normal concrete in this time range. In a comprehensive investigation of strength development of 84 concrete mixtures up to 90 days, Dagestad (37), showed a general trend for the CSF concrete to lag behind the control concrete mostly between one and seven days, at equal 28-day strengths. At early ages the filler effect of the very fine CSF particles presumably acts as an accelerator, and, by the adsorption of water-reducing agents, offsets some of their retarding effects.

For the period from 28 to 90 days the general tendency was for the CSF concrete to have a higher strength gain than the control concrete, which particularly applies to lean concrete. Johansen (33, 50) measured strength up to three years and concluded that there was little effect of CSF on either the strength gain between 28 days and one year or between one and three years for water-stored specimens. Aitcin (51) reports that, for concretes of equal 28-day strength, the CSF concrete will have somewhat lower long-term strengths, which is in contrast to the results cited previously. However, long-term water storage is of limited practical interest, and the results from dry storage are discussed later.

The problems of obtaining early strength for CSF concrete are partly overcome in practical use (ready-mixed concrete, precast production) either by using warm concrete or by applying insulation and heat-curing or both. A number of investigations on the effects of heat treatment have also been carried out. The first, by Johansen (52) on concretes mixed at 25 and 50°C, did not show higher 1- and 3-day strengths relative to 28-day strengths for CSF concrete compared to the control concrete, possibly because the high initial temperature was only maintained over a short period.

Sandvik (53) measured strength development of 25-MPa concrete with 0 and 10% CSF at 5, 20, and 40°C. The concretes were mixed at 20°C and were placed immediately at their curing temperatures; after one day they were transferred to water baths. The results showed the normal pattern at 20°C, and very slow development for CSF concrete at 5°C — even at 28 days it had only reached about two-thirds of the strength of the control concrete. However, at 40°C the 1-day strength of the CSF concrete was more than 50% higher than the strength of the control. This dramatic increase is not supported by later work. Sandvik (54) later reported strength development for 40-MPa concrete with 0 and 10% CSF, cured isothermally at 20 and 40°C. Ordinary portland cement and rapid-hardening portland cements gave basically the same result: at 20°C the CSF mixes lag behind up to 28 days; at 40°C the CSF mixtures gain strength more rapidly than the control concrete, shifting the crossing point in the strength development to about three days.

Skurdal (55) reports strength development at 20, 30, and 50°C for concrete with 0, 10, and 20% CSF, all with 28-day strengths at 20°C of about 30 and 65 MPa. Curing at 50°C reduced the 28-day strength of all the concretes by about 20% relative to curing at 20°C. A similar reduction was found for concretes cured for one day at 50°C, and then for 27 days at 20°C. The 30°C curing gave a strength reduction for the control concrete of about 10% whereas no reduction was found for the CSF concrete. The effect of temperature on early strength was similar to that found by Sandvik (54). The 30°C temperature was insufficient to produce 1-day strengths in CSF concretes equal to the control, but at 50°C the CSF concretes were about equal to the control for 30-MPa concrete, and they surpassed the control strengths for 65-MPa concrete.

Maage and Hammer (56) report a comprehensive investigation involving four cement types (OPC, 10 and 25% pfa blends, and a 15% slag blend) with 0, 5, and 10% CSF. The concretes were made at 5, 20, and 35°C and were maintained at these temperatures in water for 28 days after which they were stored at 20°C in water for up to one year. Concretes in three strength classes were made: 15, 25, and 45 MPa. The compressive strength was measured from 16 h.

For 20°C curing, the CSF had the same influence on strength development as already discussed regardless of the cement type (Fig. 4.1). Figures 4.2 and 4.3 show relative strength development at 5°C with and without 10% CSF for the four cement types, and similar data for 35°C curing is shown in Figures 4.4 and 4.5.

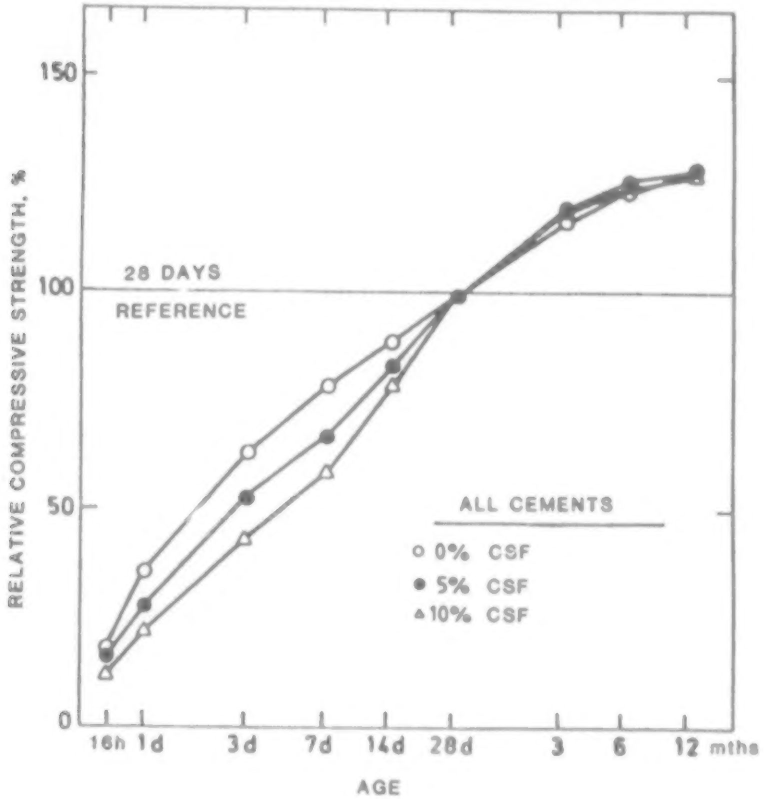

Fig. 4.1 — Compressive strength development of concrete, water-cured at 20°C, with various CSF contents. Each curve represents mean values for four cement types; 100% represents 28-day strength for each mix type (56).

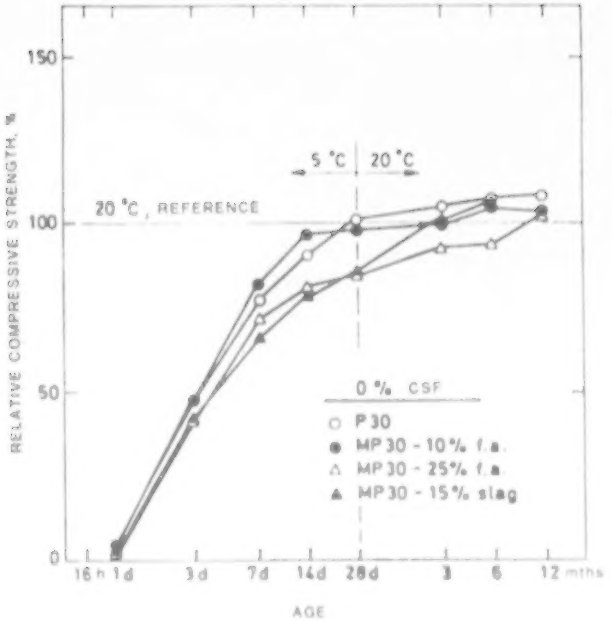

Fig. 4.2 — Development of compressive strength in reference concrete cured in water at 5°C for 28 days, then at 20°C. 100% represents 28-day strength at 20°C for each cement type (56).

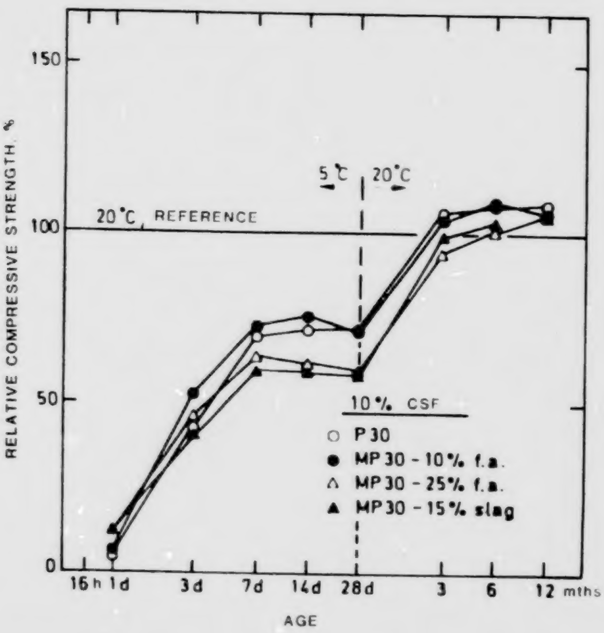

Fig. 4.3 — Development of compressive strength in concrete containing 10% CSF cured in water at 5°C for 28 days, then at 20°C. 100% represents 28-day strength at 20°C for each cement type (56).

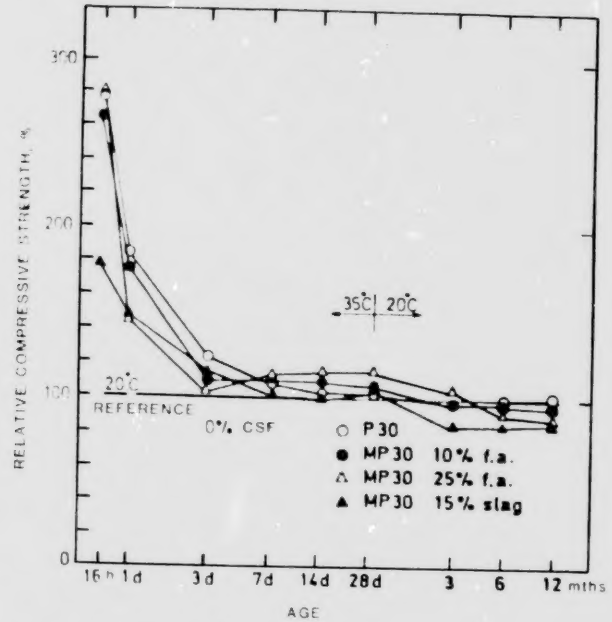

Fig. 4.4 — Development of compressive strength in concrete cured in water at 35°C for 28 days, then at 20°C. 100% represents 28-day strength at 20°C for each cement type (56).

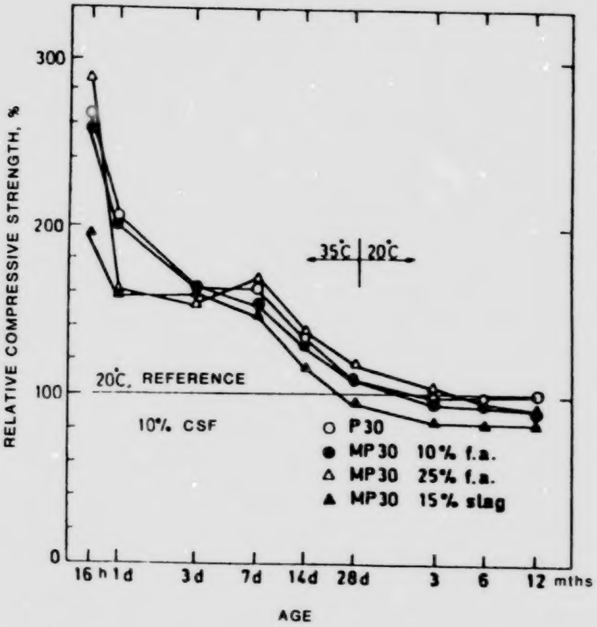

Fig. 4.5 — Development of compressive strength of concrete containing 10% CSF cured in water at 35°C for 28 days, then at 20°C. 100% represents 28-day strength at 20°C for each cement type (56).

At 5°C the blended cement concretes lag behind OPC concretes in strength development; with 10% CSF, the strength lag increases — it looks as if the pozzolanic reactions have not contributed much to strength in the 28-day period. At 35°C, the CSF concrete shows rapid gains in strength relative to 20°C curing, compared to the corresponding reference concretes.

Heat Development

Isothermal heat development data already cited, Meland (48), showed that total heat development after two days was reduced when cement was replaced 1:1 by CSF. However, during such a short period little of the pozzolanic reaction has taken place. Adiabatic measurements on concrete (57) and unpublished results, show that the heat development by the pozzolanic reaction is one-to-two times as high per gram CSF as the cement hydration per gram cement; assuming that the two chemical reactions do not influence each other in CSF concrete.

As the strength potential is several times as high per unit weight CSF as for cement, and because the heat development under normal field conditions is slower than under adiabatic conditions, it is possible to design a low-heat concrete of a specified strength using CSF as has been shown by Rasmussen (58), Skurdal (55), and Lessard et al. (59).

Conclusions: Hardened Concrete — Strength Development

The main contribution of CSF to concrete strength development at 20°C takes place from about 3 to 28 days. For CSF and control concretes of equal 28-day strength, the strength of the CSF concrete will be lower over the entire time period with 20°C curing.

Curing at elevated temperatures has a greater accelerating effect on the CSF concrete than on the control concrete. The published data indicate that a curing temperature of roughly 50°C is necessary for CSF concrete to equal the one-day strength of an equivalent control concrete.

In practice, the low strength development at early ages may be overcome either by using warm concrete and insulation or by applying heat.

The use of CSF makes it possible to proportion low-heat concrete over a wide range of strength levels.

5. HARDENED CONCRETE — MECHANICAL PROPERTIES

Compressive Strength

The contribution of CSF to concrete strength can be expressed in at least two different ways. Løland and Hustad (34, 60) introduced the term *efficiency factor* (K) defined by the equation:

$$\left(\frac{w}{c}\right)_R = \left(\frac{w}{c + K \cdot s}\right)_S$$

The subscripts R and S indicate reference and CSF concrete, respectively. The equation is based on the general assumption that, for given materials, each property of concrete is a function of the water-to-cement ratio. By applying a K-factor to the amount of CSF, it is converted into an equivalent amount of cement. The efficiency factor may be calculated for any property of concrete. It should be pointed out that K is a *marginal* quantity and, therefore, is quite sensitive to the accuracy of the test data, which is made clear by Modéer (61) who studied batch-to-batch variation for concrete with and without CSF, as well as by Maage and Hammer (56).

Another factor, the *cement replacement factor* (K_c) is defined as the difference in cement contents needed to produce equal strength in the reference and CSF concretes with the same slump, divided by the CSF content. K_c takes into account different water demands in the two types of concrete; its numerical value therefore depends on the type and amount of water-reducing agent used, which is the reason why it is considered less *fundamental* than the efficiency factor, K. The relationship between the two factors is discussed by Sellevold and Radjy (36). Examples of K_c based on the experience with the ready-mixed concrete are given by Skrastins and Zoldners (62).

Figure 5.1 shows that the general shape of the curve for strength versus the water-to-cement ratio is maintained, but is shifted to a higher level when CSF is added to concrete.

The majority of the papers published on the CSF concrete contain data on compressive strength, but only a few contain sufficient data to allow calculation of K-factors. Løland (63) analysed data from Johansen (50) and Løland and Hustad (60) found that K was equal to 2 for CSF concrete with 300 kg/m^3 or higher cement content, whereas for leaner concrete the K was equal to 3. Sellevold and Radjy (36) report K to be between 2 and 4, the highest values for rich mixtures in contrast to Løland. In line with general practical experience they also found K to be higher for 8% CSF content than for 16% by weight of cement. Sørensen (64) found the K-factors ranged from 2 to 5, increasing for richer mixtures and decreasing with higher CSF contents.

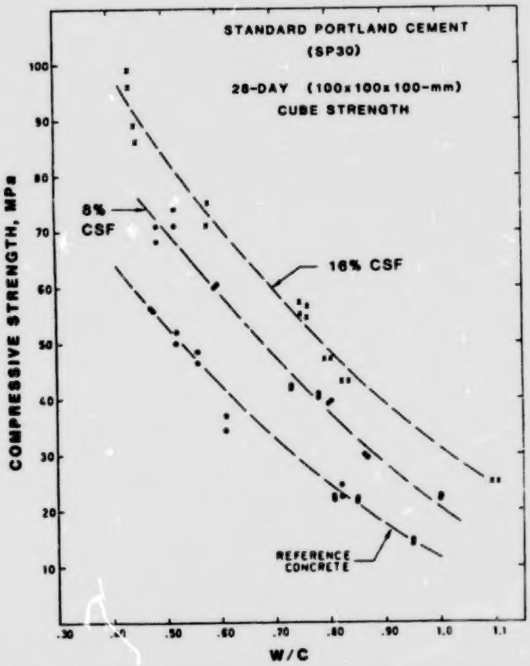

Fig. 5.1 — Compressive strength at 28 days versus water-to-cement ratio for concrete with different CSF contents. Concretes with and without water-reducing admixtures are not differentiated (36).

Strength results inconsistent with the general trend appear in the literature. For example, Carette and Malhotra (40) report strengths for concrete with ratio for W/C + S of 0.40 where from 0 to 30% of the cement was replaced by CSF. Different amounts of a superplasticizer were used to maintain workability. The 28-day compressive strength did not vary for mixtures with CSF from 5 to 20%, in contrast to the expectations based on the Norwegian results.

The strength potential of the CSF was found to vary somewhat with the cement type, (36). However, when the uncertainty in the efficiency factor is taken into account, it has been shown by analysis of results with four cement types (three blends with pfa and slag) that such differences are probably not statistically significant, (56).

Malhotra and Carette (65) have shown that low content of CSF may be used to compensate for strength reduction in blended cements with 50% slag, but only at ages above 14 days.

The use of water-reducing agents in CSF concrete, and their role in dispersing the very fine particles has often been discussed. From a practical point of view it is generally necessary to use them, because the strength-giving potential of

CSF may otherwise be offset by the increased water demand. However, there is little evidence that CSF concretes without water-reducing agents result in concrete with inferior mechanical properties as compared to the control concrete when a comparison is made on an equal W/C + S basis, (36). One exception is the flexural strength which is discussed later. Microscopic examinations, (32), have revealed different degrees of CSF dispersion in hardened concrete; however, such differences have not been related to differences in concrete properties.

The results just cited apply to water-cured concrete of 28 days or older. A number of papers have investigated the effects of early drying on strength properties. Because the major contribution of CSF to strength development occurs between 3 to 28 days, it is natural to suspect that CSF concrete is vulnerable to inadequate curing.

Johansen (33,50) and Sellevold and Radjy (36) report compressive strength development for continuously water-cured CSF concrete and for companion cube specimens exposed to laboratory air directly after demoulding. Concretes both with and without CSF suffer long-term strength loss as a result of the early drying; a reduction in the range 10 to 20% relative to water-cured companion specimens was observed. There is little difference between the two types of concrete, except possibly that the strength loss is somewhat greater for the CSF concretes of strengths less than 30 MPa, than the equivalent control concretes.

Maage and Hammer (56) found that dry-curing of 100-mm cubes made with ordinary portland cement (OPC) and 10% pfa blended cement immediately after demoulding did not reduce the strength of the concrete relative to water-cured control concrete until after six months. With a 25% pfa blend and a 15% slag blend, the reduction appeared after about 14 days of dry-curing. The 10% CSF concrete showed reduction in strength after as little as seven days curing for all four cement types. After one year, the reduction in strength for the dry-cured reference concrete was 10 to 30% depending on the cement type, whereas for the CSF concrete, it ranged from 20 to 45% reduction relative to water-cured companions. The curing was exceptionally poor in these experiments as the 100-mm cubes dried from all sides directly after exposure. A follow-up series run at three laboratories indicates that the strength losses resulting from poor curing are much reduced when the cubes are allowed to dry from one side only.

Løland and Hustad (60) found that either type of concrete wet-cured seven days before exposure to drying, suffered little strength loss, as was found by Petersson et al. (41) for concretes wet-cured for five days before exposure.

It is evident from these results that CSF concrete requires protection at early ages to realize its strength potential.

Tensile and Flexural Strength

The relationship between compressive strength and tensile, flexural, or splitting-tensile strength has been studied by some investigators. Løland and Hustad (60) report direct tension and flexure data for CSF concrete, continuously water-cured or exposed to drying after seven days in water. Ages at the time of test were about three months for the water-cured samples and one year for those exposed to drying. Løland and Gjørv (66) plotted the results as tensile strength versus compressive strength for both curing conditions. The plot reveals that dry-stored specimens without CSF have a higher ratio of tensile to compressive strength than wet-stored specimens. For CSF concrete, the curing condition has no systematic influence, and the curve falls in between the two curves for the control concrete. Flexural strength test results follow the same pattern as the test results for tensile strengths.

Johansen (33, 50) reports both compressive and flexural strength data for concrete exposed to drying upon demoulding. Ages at the time of the test were one and three years. There was little overall change in either strength property from one to three years, and no significant influence of CSF was found. A plot of flexural versus compressive strength showed that the same relationship was valid for concrete with 0 and 5% CSF both with and without water-reducing admixture. Concrete with 11% CSF and a water-reducing agent also followed the same relationship, but the 11% CSF concrete without a water-reducing admixture and 25% CSF concrete both with and without water-reducing admixtures had lowered the ratio of flexural strength to compressive strength.

Maage and Hammer (56) measured tensile strength for concrete with four cement types and various CSF contents, both water-cured and exposed to drying after demoulding. Water-cured CSF concrete uniformly produced higher tensile strengths, for given compressive strengths, than did reference concrete for all types of cement. After three months of dry-curing, the concrete made with blended cement performed significantly worse (15 to 35%) than the companion water-cured specimens, whereas the OPC concrete only suffered a small reduction in tensile strength due to dry curing. Thus, the tensile strength of concrete made with blended cement, or any cement with CSF, is very sensitive to curing conditions. Figure 5.2 shows that all concretes tested result in more or less similar curves for the two curing conditions in a plot of tensile versus compressive strength. (Note that the over-all plot in Figure 5.2 shows a general trend, but obscures the detailed results discussed.) Figure 5.2 is in contrast to the behavior when dry-curing is preceeded by seven days of water-curing as previously discussed (66). Although the picture is not entirely clear at present, it does indicate that the early curing history is important. Dispersion may also play a role as concretes without plasticizers were more sensitive to poor curing than were those containing plasticizers. This finding applies to concretes of equal compressive strength.

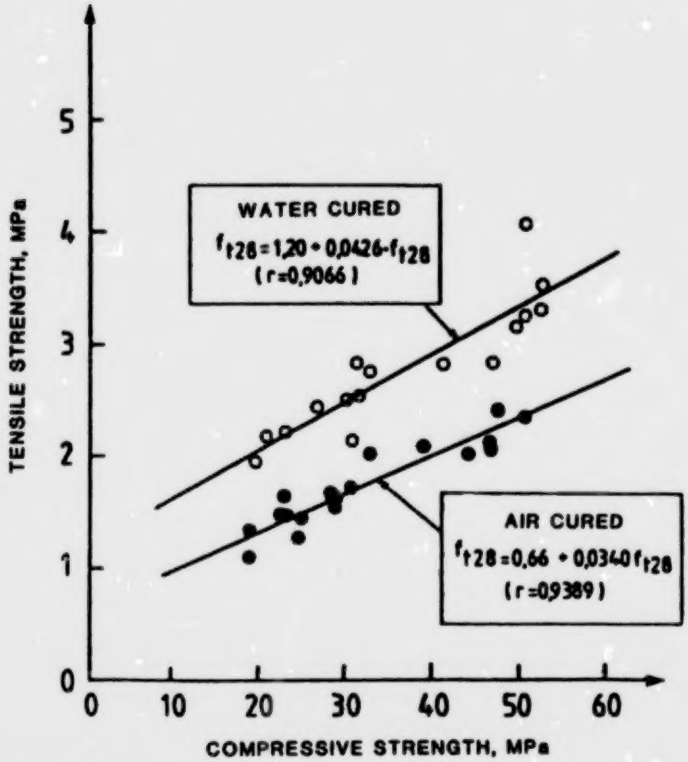

Fig. 5.2 — Relationship between compressive and tensile strengths for water-cured samples (°) and samples exposed to drying in air from the point of demoulding (•). Four cement types, and 0 and 10% CSF contents are included (56).

Brittleness, E-modulus

Cement pastes with more than 10% CSF have been found to be brittle, (6, 67). Principles of fracture mechanics have been applied to study brittleness or ductility in CSF concrete. Løland and Hustad (68) compared ductility of 25-MPa concrete with 0 and 10% CSF by weight of cement, and concluded that the difference was very small, with a tendency to somewhat lower ductility in the CSF concrete. A more comprehensive study by Løland (69), reviewed later by the same author (63), covered many grades of concrete as well as wet- and dry-curing. A plot of *maximum fracture zone deformation* versus tensile strength did not reveal any systematic difference between the CSF and the control concretes. The curing condition had an influence, but the major effect was, as generally agreed, that increased strength led to increased brittleness.

Tunnel segments of high-strength concrete (>80 MPa) with CSF were produced to protect gas pipelines on the western shore of Norway. Details of the project, including stress–strain diagrams for the concrete, were reported by Einstabland et al. (70). The stress–strain curves were almost linear up to 0.2% strain, with a fracture strain of close to 0.3%. More complete stress–strain diagrams, using a very stiff testing machine designed for high-strength and very high-strength (>100 MPa) concrete with CSF, was reported by Helland et al. (71). They found that as the strength increased, the fracture strain also increased. But also that the *falling* part of the stress–strain curve increased in steepness (Fig. 5.3). This is in line with experience with normal concrete. A brittle concrete does not necessarily mean a brittle construction; that depends on design and reinforcement. Helland et al. (71) also reports test data for overreinforced beams, which did not disintegrate, but which failed gradually, presumably because the compressive failure was local and spread progressively inwards in the cross section.

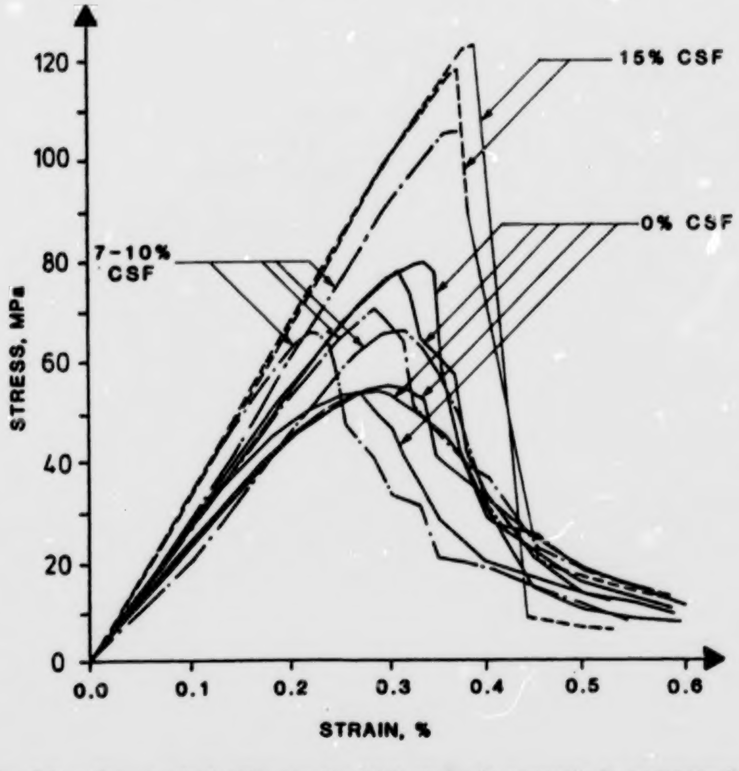

Fig. 5.3 — Stress–strain diagram for high-strength concrete in compression.
Key: ——— = *0% CSF*
—·— = *7–10% CSF*
– – – – = *15% CSF, basalt aggregate (71).*

The high failure strain of the very high-strength CSF concrete is a consequence of the fact that the Young's modulus of elasticity, E, does not by far increase as much as the compressive strength. Løland (63) gives data for E-modulus versus compressive strength for a large number of concretes demonstrating this. He finds no significant difference between the CSF and control concretes. Sellevold et al. (6) showed that the dynamic E-modulus of cement pastes increased with the increasing CSF addition. In concrete, however, the aggregates dominate the E-modulus. Hence, increased stiffness of the binder phase is reflected only to a moderate degree in concrete.

Fly Ash–CSF Combinations

Several investigators have explored the possibility of using CSF in combination with fly ash. The purpose has generally been to use the highly reactive CSF to compensate for the slow strength development associated with fly ash in concrete. Results by Carette and Malhotra (72) confirm this possibility. Other investigations include Mehta and Gjørv (29), Dagestad (37), Rasmussen (58), Regourd et al. (73), Tendal and Sanne (74), and Carles-Gibergues et al. (75).

A relevant question in Norway has recently been CSF effects in concrete made with fly-ash blended cements. The blended cement is finely ground so that strength development matches that of ordinary portland cement. A wide range of properties of CSF concrete made with such blended cement is being studied; results have been reported by Maage et al. (39, 56). They do not indicate any significant difference in CSF effects in concretes containing ordinary portland cement or a blended cement containing 10% fly ash. Results for blended cements containing 25% fly ash show greater sensitivity to curing temperature and curing condition as already discussed.

Bond Properties

Bond properties of concrete include bond to aggregates, bond to reinforcing steel, bond to fibers, and bond when fresh concrete is placed on an old concrete.

Johansen and Dahl (76) investigated concrete-to-concrete bond for various combinations of normal and CSF concrete. They concluded that CSF was "an important aid material to obtain good bond at joints or for two-layer construction." One contributing reason for this is that segregation is small in CSF concrete. Hence, a weak top layer as a result from a horizontal placement is avoided.

Carles-Gibergues et al. (77) have studied the zone (*aureole*) formed between aggregate and cement paste. This zone is a point of weakness, being available for crack propagation in concrete. They reported that the characteristics of the aureole were altered in the presence of CSF. In particular, it reduced the thickness of the zone. Regourd (2) observed an "excellent cement paste-aggregate bond" in mortars with CSF. Part of the reason for an improved bond phase is presumably the greater stability of the CSF mixtures.

Bürge (78,79) reports improved bond strength to reinforcing steel by the use of CSF both for high-strength light-weight concrete and for high-strength normal-weight concrete.

Bache (80) reports high bond strength to plastic fibres in a review of ultra high-strength CSF concretes, as do Krenchel and Shah (81). Ramakrishnan and Srinivasan (82) studied steel fibre–reinforced concrete and found that in general, CSF improved the performance characteristics of steel fibre–reinforced concrete.

Scandinavia has recently seen the widespread use of steel fibre–reinforced shotcrete using the wet process, as this makes it possible to avoid wire mesh reinforcing nets. A recent comprehensive study of field projects with laboratory follow-up, (83), concluded that CSF is an important ingredient in the mixture, but because of lack of control in field situations the effects of CSF are difficult to quantify. The need for an accelerator in CSF mixes to maintain low rebound losses, appears to have been reduced. The use of this method in the United States is reported by Corwine (84).

The use of CSF in carbon fibre–reinforced cements has been investigated by Ohama et al. (85). They conclude that the CSF plus water-reducing admixtures are efficient for dispersing the carbon fibres, and that the CSF improves fibre anchorage.

Bergstrøm and Gram (86) used CSF to reduce the pH in the pore water of the cement matrix to improve the durability of alkali-sensitive fibres. They concluded that embrittlement was delayed, but was not prevented for glass fibres. For sisal fibres they found that embrittlement "can be avoided almost completely."

Experience with CSF in asbestos-free fibre-reinforced cement is reported by Radjy et al. (87).

All these studies indicate that CSF can be used to improve the bond as well as the durability properties.

Shrinkage

Traetteberg and Alstad (88) measured shrinkage of pastes with W/C + S of 0.50, with 0, 5, and 15% of the cement replaced by CSF. The pastes were cured for either 2 or 28 days before exposure to relative humidities from 12 to 75%. For samples exposed after two days of curing the results indicated greater shrinkage at increasing CSF contents. This result was particularly significant at RH values below 50%, i.e., in a range below that at which concrete shrinkage normally is assessed. The same trend was observed for pastes precured for 28 days. The weight loss of the CSF pastes was less than for the control pastes in the *capillary range*, i.e., at RH values above about 40%.

In assessing these observations it may be noted that the pastes were made with constant W/C + S: the CSF pastes have finer pore structure and, consequently, retain more capillary-condensed water at a given RH. At RH values below the capillary range, the weight loss and the shrinkage is controlled by the amount of CSH, which is greater for the CSF pastes.

The shrinkage of concrete of course depends on the shrinkage of the cement paste, but also very much on the volume fraction of the aggregate. Several investigations have been made of shrinkage in concrete by standard methods, i.e., unrestrained shrinkage of prismatic specimens at RH of 50 to 60%.

Johansen (33, 50) measured shrinkage on concrete prisms exposed to 50% RH directly after demoulding and after 28 days of water-curing. The W/C + S varied from 0.37 to 1.06, and the CSF content from 0 to 25% by weight of cement. The mortar fraction was also sieved from the fresh concrete and parallel shrinkage measurements were performed on mortar prisms. The concretes were produced with predetermined cement plus CSF contents both with and without water-reducing admixtures. The water demand to produce the desired slump, therefore, varied widely, resulting in varying W:C + S ratios as well as varying aggregate volume fractions. It is therefore difficult to compare the measured shrinkage values directly. For samples precured for 28 days and with 0, 5, and 10% CSF, the shrinkage values at three years varied little and were not directly related to either water-reducing admixtures, aggregate volume fraction, or the W/C + S. At 25% CSF content the influence of water-reducing admixtures was evident in that they produced significantly higher aggregate volume fractions and, therefore, lower shrinkage over the entire W/C + S range. This applied to both 1 and 28 days of precuring. In general, only one day of precuring resulted in higher shrinkage, particularly for CSF concrete and for control concrete with W/C less than 0.60. Thus, for quality concrete (W/C + S <0.60) no significant difference was found between the control concrete and concrete containing 0, 5, and 10% CSF. The 25% CSF concrete produced higher shrinkages, particularly concrete with no water-reducing admixtures. Shrinkage data on mortars generally followed the same pattern, with a small tendency to increased shrinkage with increasing CSF content up to 10% and a clearly significant difference at 25% CSF content.

Johansen (33) applied a simple, composite model to relate the shrinkage values for the concretes and for their equivalent mortars. He found that increasing CSF content led to a lower ratio between concrete and mortar shrinkage, and concluded that this difference must be caused by a higher degree of stress relaxation in CSF concrete, because the shrinkage potential in the mortars was not fully reflected in concrete shrinkage. He also suggested that this might be caused by increased microcracking in CSF concrete. As discussed elsewhere in this chapter, microscopic studies of field CSF concretes have suggested a higher density of microcracks than in control concrete, Christensen (32). The importance of such microcracking for concrete properties has not been established, so the implications are, as yet, unclear.

Løland and Hustad (60) measured shrinkage for 25 concrete mixtures, with 0, 10, and 20% CSF by weight of cement and W/C + S from 0.37 to 2.11. The specimens were exposed to 60% RH after seven days of moist-curing. The shrinkage after 14 months was not significantly different for concretes with W:C + S ratios over 0.60. At lower values the concrete containing CSF had less shrinkage than the controls.

Carette and Malhotra (40) moist-cured the concrete for 28 days and subsequently measured shrinkage 84 days after production. Two series were tested: one using about 230 kg cement plus CSF, with CSF content from 0 to 43%. No water-reducing agent was used, hence the W:C + S ratio varied from 0.64 to 0.84 with increasing CSF content. The other series had the same range of CSF content, but the cement plus CSF was kept constant at about 400 kg/m^3 and the W/C + S at 0.40 by using different amounts of a superplasticizer. For both series the pattern was less shrinkage for the concretes containing CSF. The measuring time was very short in these experiments, which may have distorted the results. For example, Maage (89) has reported shrinkage with 0 and 10% CSF concrete cured 28 days prior to exposure, where shrinkage for the CSF concrete was less than for the control of equal strength at times up to several months, but then tended to increase. When exposed immediately after demoulding, the CSF concrete showed somewhat greater shrinkage over the whole time span. Maage's experiments were performed both with OPC and with a blended cement with 10% fly ash interground. The shrinkage properties of the two cements did not differ.

Malhotra and Carette (65) measured shrinkage up to 100 days in slag–cement concretes containing CSF and found only marginal differences relative to the control concrete.

Petersson et al. (41) measured shrinkage after seven days of wet-curing for concretes with 0, 7, and 13% CSF content by weight of cement. The concrete mixtures were lean with W/C + S ranging from 0.80 to 0.94, and 28-day compressive strengths ranging from 27 to 35 MPa. At short curing times the CSF concrete had higher shrinkage, but at curing times exceeding 80 days, there was little difference from the control.

Buil and Acker (90) measured shrinkage of a control concrete (W/C = 0.44) and one containing 33% CSF (W/C + S = 0.40). The CSF concrete had shrinkage strains roughly one-half as large as the control concrete after about one year. For high-strength mortars with and without 40% CSF, Buil et al. (43) found slightly higher shrinkage after 90 days for the CSF concrete (99 MPa) than for the control concrete without a superplasticizer (50 MPa), whereas a control concrete (63 MPa) with the same superplasticizer content as the CSF concrete had almost twice as high shrinkage.

For a series of very high-strength concretes with CSF Helland et al. (71) measured shrinkage according to ASTM C 157. They found low shrinkage values compared to normal concretes, and that shrinkage was linearly related to the water content of the concrete.

Wolsiefer (91) has also reported shrinkage for high-strength (>100 MPa) CSF concrete. For samples moist-cured for 14 days prior to exposure (ASTM C 157) lower shrinkage was observed than for reference concrete, whereas exposure after one day led to higher shrinkage for CSF concrete.

It appears from the existing evidence that at equal W/C + S the CSF paste has a higher shrinkage potential than a control paste. This effect is most evident at CSF contents above 10% by weight of cement, as also seen in mortar tests.

The effect of exposure to drying early on is less clear; pastes with or without CSF showed little sensitivity, whereas mortars showed a clear tendency to increased shrinkage upon early drying. This tendency was of the same magnitude for mortars with 0, 5, or 10% CSF.

Shrinkage data for concrete are even more difficult to assess because the volume fraction of aggregates plays an important role, and in laboratory experiments this variable is not usually optimized. Minimum shrinkage is obtained when the binder phase volume fraction is minimum, and its quality is maximum (low W/C + S). Hence, the use of water-reducing admixtures is important in that it allows reduction in the binder phase volume fraction. However, water-reducing admixtures by themselves lead to increased shrinkage, thus offsetting some or all of the advantage gained by the reduced water content.

The results reviewed here indicate that concrete shrinkage is little influenced by CSF contents at least up to 10% by weight of cement. For concrete exposed to early drying, increased shrinkage is most marked for lean CSF concrete (W/C + S >0.60) and for high CSF contents (>10% by weight of cement). This result seems natural, because early drying inhibits the pozzolanic reaction.

CSF concrete dries out slower than control concrete of equal strength, which may partly explain why the higher shrinkage potential in CSF-containing cement paste is not reflected in concrete shrinkage. It is known that slow drying (or large specimen size) leads to decreased shrinkage for a given concrete.

Finally, it should be noted that crack sensitivity of concrete is not only related to shrinkage, but to the creep and stress relaxation properties as well. Data on shrinkage alone are, therefore, of limited value in connection with crack sensitivity.

Creep

Only two reports are available on creep of CSF concrete. Buil and Acker (90) measured drying creep and creep in a sealed environment for a control concrete (W/C = 0.44, 53 MPa) and one with 33% CSF (W/C + S = 0.40, 76 MPa). However, the sealing was apparently not very efficient because unloaded sealed samples also suffered substantial strains. The creep of the sealed specimens was roughly equal for the two types of concrete, whereas the CSF concrete had substantially less total creep deformation under drying conditions than did the control.

Wolsiefer (91) measured creep of CSF concrete. High-strength concrete test specimens were loaded at 12 h and at 28 days. Wolsiefer reports that up to four months the CSF concretes showed less creep than data reported for normal high-strength concrete.

Fire Resistance

Aaneland (92) exposed one face of concrete elements to ISO (wood fire) and HC (hydrocarbon) fire loads. Four concretes were tested, one of which contained 9% CSF by weight of cement. The 28-day cube strengths for the four concretes were 32 to 35 MPa. The elements were tested at 12 weeks of age. All elements fulfilled the requirements to temperature on the unexposed side. Spalling on the exposed side was also evaluated. The CSF concrete exhibited somewhat higher spalling, but the data were too limited to allow general conclusions to be drawn.

Pedersen (93) exposed 100-mm cylinders of ultra high-strength CSF concrete ($W/C+S = 0.16$ and 20% CSF) to slow heating (1°C/min). Several of the specimens suddenly disintegrated at temperatures near 300°C. It should be kept in mind that the mix-proportioning used was extreme and is by no means representative for CSF concrete. However, certain characteristics of CSF concrete are important in connection with the spalling problem. CSF concrete dries out very slowly, whereas its thermal conductivity probably is as high as, or higher than, that for normal concrete. These factors indicate that high vapor pressure can be built up internally and can cause spalling. Hertz (94) has discussed the question in connection with dense CSF concrete.

The residual strength of CSF concrete after heating to 530°C has been investigated by Dahl (95). Increasing the content of CSF resulted in somewhat reduced temperature resistance, whereas water storage after heat exposure led to large strength gains for mixes with 0 and 10% CSF. Mixes with 20% CSF experienced lower strength gains.

From the above it appears that spalling, particularly in connection with structural high-strength CSF concrete is a problem that needs further research.

Abrasion–Erosion Resistance

Mortars having very low water-to-cement ratio (<0.25) and high CSF contents (>20%) are known to be highly resistant to abrasion and wear. This property is of use in a variety of applications. For concrete, few published data are available. Holland (96) has reported on a repair project using high-strength CSF concrete on the Kinzua Dam stilling basin. Laboratory results on abrasion erosion were very promising and repairs were carried out in 1983 after full-scale tests had been made. A follow-up report after one year service states that "the concrete appears to be performing as intended" (161).

Conclusions: Mechanical Properties

The contribution of CSF to any property of hardened concrete may be expressed in terms of an *efficiency* factor, K. The K-factor is a marginal quantity that cannot normally be determined very accurately. For compressive strength the K-factor is in the range of 2 to 5, meaning that 2–5 kg cement may be replaced by 1 kg CSF in a given concrete without impairing the compressive strength. This applies provided the water content is kept constant and the CSF content is less than about 20% by weight of cement. The CSF makes it possible to produce very high-strength concrete (over 100 MPa) on a routine basis.

Tensile and flexural strengths of CSF concrete are related to compressive strength in a manner similar to that of normal concrete. However, if CSF concrete is exposed to drying after only one day of curing, the tensile and flexural strengths are reduced more than those for control concrete.

The brittleness of conventional concrete increases with increasing strength level. The CSF concrete appears to follow the same pattern as conventional concrete in this respect.

Data reviewed indicate that CSF can be used to improve the bond of concrete to aggregate, to reinforcing steel, to various fibers, or to old concrete.

Cement paste and mortar containing CSF appear to have a larger shrinkage potential than controls at equal W/C + S. This increased potential has not been found to be reflected in increased concrete shrinkage.

CSF concrete has the same thermal conductivity as normal concrete, but a lower permeability to water vapor. Fire exposure tests indicate that CSF concrete is more vulnerable to spalling than normal concrete.

High-strength CSF concrete has superior abrasion, erosion, and wear resistance properties as compared to conventional concrete.

6. HARDENED CONCRETE — DURABILITY

A substantial number of papers have been published on various durability aspects of concrete containing CSF. Review papers have been presented by Hjorth (1), Gjørv (97), and Vennesland and Gjørv (98).

A general agreement exists that, apart from its chemical composition, the permeability of a given concrete is a good indicator of its durability under conditions of physical and chemical attack. Thus, data on the permeability are discussed first in this section.

Permeability

The term *permeability* may be applied to gas, vapor, and liquid transport through a porous material, although, when describing gas or vapor, the term *diffusion* is generally more used. Two types of experimental techniques have been used with the CSF concrete and cement paste:

— observation of weight loss versus drying time;

— water transport under a pressure gradient.

Oxygen and chloride diffusion in water-saturated concrete have also been measured, but are discussed in connection with corrosion of reinforcement.

Drying experiments

Sellevold et al. (6) measured drying rates for 3-mm thick discs of cement–CSF pastes, containing from 0 to 20% of CSF by weight of cement. One series, in which the water-to-cement ratio was kept constant and the CSF was used as an additive, showed that the relative diffusion coefficient was reduced from 1.0 at 0% CSF to 0.25 at 20% CSF. The reduction was non-linear, i.e., the effect per unit weight of CSF added decreased with increasing total CSF content. A parallel series in which the water content in the paste was kept constant and the cement was replaced by CSF in a ratio of 3:1, gave equal diffusion coefficients for 0, 8, and 16% CSF contents by weight of cement. This result indicates that with respect to the water diffusion during drying the efficiency factor (K) of the CSF in cement paste is about 3, close to the value of K generally found for compressive strength.

Sørensen (64) calculated relative diffusion coefficients from drying experiments on concrete discs containing 0, 8, and 16% CSF by weight of cement. The efficiency factor for the CSF with respect to drying calculated from these results was in the range 6 to 8, i.e., higher than K for compressive strength.

The two investigations considered together show that the CSF has a greater effect in concrete than in cement paste, indicating that the boundary phase between aggregate and paste is improved more by the use of CSF than the cement paste phase itself. This finding has implications for any other property of concrete that depends on the quality of the interface, for example, bond and water permeability.

Water permeability

The first permeability tests on the CSF concrete were carried out in the 1960's by Markestad (99). Using a lean mix (W/C = 0.89), and replacing 20% of the cement with CSF, the concrete was found to be *completely impermeable* to water under seven atmospheres of pressure for 15 days (60-mm-thick disc specimens). In 1975, water penetration tests according to Swedish Standard were carried out on concrete with 0, 10, and 20% CSF replacement of the cement on a 1:1 basis, (100). The results gave higher strengths for the CSF concretes, and about one-half as much water penetration in the 10% CSF concretes compared with the reference concrete. The 20% CSF reduced the penetration further, but substantially less than twice the value that was obtained with the 10% CSF. Note that no water-reducing admixture was used in either of these investigations.

As part of a comprehensive investigation, the water permeability of 25 concretes was measured by Hustad and Løland (101). The concretes contained 0, 10, and 20% CSF by weight of cement and were made both with and without water-reducing admixtures. The cement content ranged from 100 to 500 kg/m^3. When comparing permeability coefficients on the basis of the same 28-day compressive strength, the CSF concretes were somewhat less permeable at strength levels up to 30–40 MPa. At higher strength levels the sensitivity of the test method used was not high enough to permit comparisons, and all concretes were essentially *watertight*. The permeability coefficients for the high-strength concretes were in the range 10^{-13} to 10^{-15} m/s.

Sandvik (57) has reported permeability coefficients for concretes of fixed composition except for 5, 10, and 20% replacement of cement by CSF on a 1:1 basis. The reference mix had 300 kg/m^3 of cement and a 28-day cube compressive strength of 31 MPa with the CSF concretes having strengths for increasing CSF contents of 36, 43, and 44 MPa, respectively. No water-reducing admixtures were used. The results do not permit comparison at equal strength levels. The 5% CSF produced a reduction in the permeability coefficient from 3×10^{-11} to 6×10^{-14} m/s; at higher CSF replacement levels the coefficient was too low to be measured, i.e., below 10^{-14} m/s.

Skurdal (55) measured permeability coefficients of a reference concrete and one containing 10% CSF by weight of cement. Both concretes had 28-day cube compressive strengths of about 32 MPa at 20°C curing. Parallel samples were cured at 30°C and 50°C. The curing at 30°C resulted in slightly lower strengths at 28 days, whereas curing at 50°C led to reductions of about 20% for both concretes. The permeability coefficients of the CSF concretes were consistently lower than for the reference concretes (20°C curing: 7.2×10^{-13} and 0.5×10^{-13} m/s; 30°C curing: 27×10^{-13} and 0.8×10^{-13} m/s; and 50°C curing: 90×10^{-13} and 74×10^{-13} m/s). Heat curing of both types of concrete led to increased permeability.

The values for the permeability coefficients in the two latter investigations do not match precisely for comparable concretes, in spite of the fact that the same experimental apparatus was used. This phenomenon is common for permeability measurements, and emphasizes the need for caution when one, for example, attempts to base evaluations of the effects of CSF on results from different test series.

As part of a project to investigate the condition of field concretes with and without CSF, Maage (102) measured the water permeability of discs cut from drilled cores in various structures. The age of the structures varied from three to nine years. The results are shown in Figure 6.1. The abscissa is (water/cement + 3x (silica fume)) to compare concretes of similar compressive strengths. The trend is that the CSF concretes have lower permeability at equal strength. Microscopic examination of thin sections from the concretes was made at the Technological Institute in Denmark where it was concluded that CSF mixes in general were more dense, and that they contained more microcracks. The microcracks apparently have no influence on the permeability, nor on the measured stress–strain curves in compression.

In a comprehensive test series of CSF with blended cements already described (56), permeability was also measured (103). The results were not entirely consistent, but, on average, the CSF concretes had somewhat lower permeability than control concretes at equal strength. The CSF appeared to have least effect with a blended cement containing 25% fly ash. The concretes were water-cured for an initial period of 28 days and were then exposed to six months of air drying prior to testing. It has already been discussed that drying and rewetting treatment *opens* the pore structure of cement paste and, in particular, CSF cement pastes (6). Johansen (104) found that the permeability

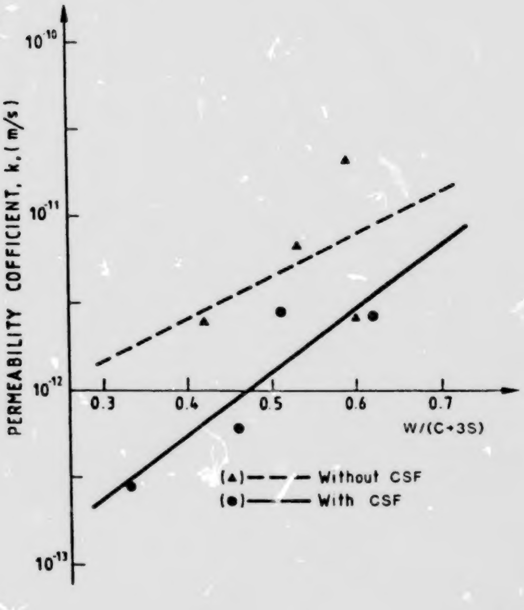

Fig. 6.1 — Permeability of samples drilled from structures. W/C for controls and W/(C+3S) for CSF concrete (102).

increased more for the CSF concrete than for the control concrete after such a drying and rewetting treatment.

Mindess and Gray (105) report on a permeability study of CSF and control mixtures, testing both pastes and cement–aggregate composites. They conclude that CSF appears to decrease the permeability. However, the presence of aggregate was not found to have much influence on permeability, possibly because the aggregate–paste interface was too small compared to that of normal concrete, and because the great uncertainty associated with permeability measurements prevented the detection of any interface effects.

Conclusions: permeability

The available data indicate that the CSF in concrete reduces the permeability more than it improves the compressive strength, i.e., that the efficiency factor is greater with respect to permeability than with respect to compressive strength. This finding appears to be particularly evident for low content levels of CSF, and at low concrete strength levels.

A comparison of cement paste and concrete results indicates that it is particularly the aggregate–paste interface which is improved by the CSF.

Frost Resistance

The need for more durable concrete, in particular, concrete with improved resistance to freezing and thawing exposure in the presence of salts, has been the motivation for a number of investigations involving CSF concrete. These investigations include studies of air-void system characteristics, basic studies of ice formation and pore structure, as well as freezing and thawing testing with and without deicing salts.

Air-entrainment

As a part of a large study of air-entraining admixtures in concrete, Okkenhaug and Gjørv (106) and Okkenhaug (107) have studied the effects of mixer type, mixing time, aggregate grading, and air contents on the stability of the air content during handling of the concrete. Also air-void system characteristics for concrete both with and without CSF were studied. Their conclusion was that a desired total air content could be obtained relatively easily in both types of concrete, by adjusting the content of air-entraining admixture. Compared to the control concrete, the needed dosage in CSF concrete without a water-reducing agent is higher, but with a water reducer the difference is decreased. Okkenhaug (107) also concluded that for a given air content the air-void characteristics in CSF concrete are more favorable, and the air content is more stable with respect to vibration of the concrete, particularly in mixtures with both water-reducing admixtures and air entrainment.

Carette and Malhotra (40) found that for low W/C + S (0.40) the replacement of cement by CSF at 1:1 led to an increased demand of an air-entraining admixture. The mixtures also contained a superplasticizer. The air-void characteristics were measured on the hardened concrete, but in contrast to Okkenhaug and Gjørv (106), who used 8% CSF by weight of cement, the results did not indicate any consistent improvement. The use of 5% CSF did improve both the spacing factor and the specific surface, but higher CSF content led to less favorable values than for the control concrete.

Virtanen (108) found that CSF concrete needed a higher addition of air-entraining admixtures than the control concrete to reach a given air content; but that the amount was less than that required for concrete containing fly ash and slag. A plot of spacing factors versus air content for the various concrete mixtures, produced identical curves.

In a further test series, Virtanen (109) investigated concrete (40–50 MPa) for bridge edge beams, containing from 0 to 16% CSF and different amounts of air-entraining admixtures. For a given dosage of an air-entraining admixture, an increase in CSF content resulted in reduced air content in the fresh mixture. No measurements were made of the air-void parameters in the hardened concrete.

Lehtonen (110, 111) studied concrete of W/C + S = 0.45 with 0, 5, 10, and 15% CSF and found that more air-entraining admixture was needed to produce equal amounts of air with increasing CSF content. In agreement with Okkenhaug (107), he found that the air content in CSF concrete was more stable with respect to vibration. In contrast, both Aitcin and Vezina (112) and Rasmussen (113) report somewhat greater loss of air from CSF concrete during handling and placing, than for concrete without CSF.

Christensen and Jensen (114) report results of a comprehensive quality control program on concrete ($W/C+S = 0.35$, 15% CSF) for bridge edge beams. The requirements were minimum 3.5% air, specific surface of air pores more than 30 mm^{-1}, with a maximum spacing factor of 0.20 mm. The results of the program were that 28% of the concrete tested did not fulfil the air requirement, 10% failed the requirement of specific surface, although all tests gave satisfactory spacing factors. The authors conclude that the requirements of the air-void system in hardened concrete should be in terms of the most directly measured values; air content relative to the paste volume, and the specific surface area of the air-void system. Mathematically derived quantities, such as the spacing factor, are based on a number of assumptions usually not justified.

As part of a large project concerning the effects of CSF in blended cements, air-entraining of CSF mixes has been investigated by Maage and Dahl (39). Pure portland cements were used as well as 10 and 25% fly ash blends and a 15% blast-furnace slag blend. The CSF contents were 0, 5, and 10%. The mixtures were proportioned to produce equal 28-day strengths at two strength levels of 25 and 45 MPa. An attempt was made to produce realistic mixture proportions — not straight cement replacement by a certain factor. The results showed that the CSF content had remarkably little effect on the amount of air-entraining admixture needed. The response of the concrete to handling was simulated using a drum mixer and vibration treatment. The results also indicated that CSF also had little effect on the stability of the air content.

In summary, the present evidence indicates that proper air-entrainment in CSF concrete can be obtained as easily as in ordinary concrete. The air-void parameters may not improve, but will depend on all the factors involved in the production of concrete. The stability of the air-void parameters to handling and vibration of the concrete may be improved by the CSF, but this again depends on mixture-proportioning.

Large variations experienced in air-entrainment of fly ash concretes are not found in concrete containing CSF.

Moisture conditions

The moisture history and condition of a specimen is of particular importance to its frost resistance. It has been established by Fagerlund (115) that a given concrete possesses a *critical degree of saturation* (CDS) above which it is susceptible to rapid deterioration under freezing and thawing conditions, and below which deterioration is very slow. The CDS is considered a material property; to assess the frost resistance of a concrete in a given environment it is necessary to know moisture content in practice. This measurement is normally done by capillary suction experiments in which pre-dried specimens are exposed to water and the weight gain versus time is measured. The weight normally increases rapidly during the first day or two until it levels off; following this the increase is slow and presumably represents filling of air voids. The method allows the prediction of service life, i.e., equivalent to the time needed to reach the CDS.

Investigations by Vuorinen (116) have resulted in a Finnish National Standard (SFS 4475) in which the *pore protection factor* is defined as the ratio between the unfilled pore space after capillary suction and the total pore space available to water (determined by pressure saturation at 150 atmospheres). Empirical data suggest that the pore protection factor should be at least 0.25 for concrete exposed to severe conditions.

It is implicit in these methods that the concretes are exposed to drying and rewetting treatments. Sellevold and Bager (117) have established by low-temperature calorimetry studies that even mild drying (58% RH) and rewetting alters the pattern of ice formation in cement pastes and mortars quite dramatically. Freezing in virgin specimens with a water-to-cement ratio of less than 0.50 is gradual over a wide temperature range. But, after drying (at elevated temperatures) and rewetting, more ice forms, and the ice formation is concentrated in the period right after the first nucleation. Thus the drying and rewetting implicit in the Finnish and the CDS methods are not unrealistic in practical terms, and the effects of moisture condition should be taken into account in any practical frost-resistance testing.

Calorimetric determination of ice formation in hardened cement pastes with various amounts of CSF were made by Sellevold et al. (6). They found that a control paste with a water-to-cement ratio of 0.6 had a large *primary* freezing peak near 0°C, indicating, as expected, poor frost resistance. Addition of 8% or more CSF resulted in an absence of the primary freezing peak — the first freezing now taking place around -20°C. This behavior was interpreted as a result of altered pore structure in the paste. However, when pastes without primary freezing peaks were dried gently (at 58% RH) and were resaturated with water, a distinct, primary freezing peak appeared — as had also been found to be the case for control pastes (Figs. 6.2 and 6.3). Experiments have shown (118) that pastes with extremely low ratios of water to cement and high CSF contents do not give any primary freezing peaks even after drying and resaturation treatment. Thus, the present evidence indicates that it is possible to produce CSF concrete which is frost resistant without air-entrainment, provided the water-to-cement ratio is low enough and the CSF content high enough. An estimate of the required mix proportion would be a water-to-cement ratio of about 0.30 with a CSF content of 10% or more by weight of cement. Industrial trials to confirm this are being undertaken by the Danish Road Authority and others (119,120).

Two recent studies have investigated the moisture state of CSF concrete in connection with frost-resistance tests. Virtanen (109) determined the *protective pore ratio* for a series of concretes with different air contents and CSF contents of 0, 4, 8, and 16%. For a given air content the protective pore ratio increases with increasing CSF content. For example, at 6% air the ratio increases from 0.25 in the reference concrete to 0.70 for the one containing 16% CSF. Thus, the absorption of water is much slower in CSF concrete, and possibly air voids remain empty after a fixed period of water suction.

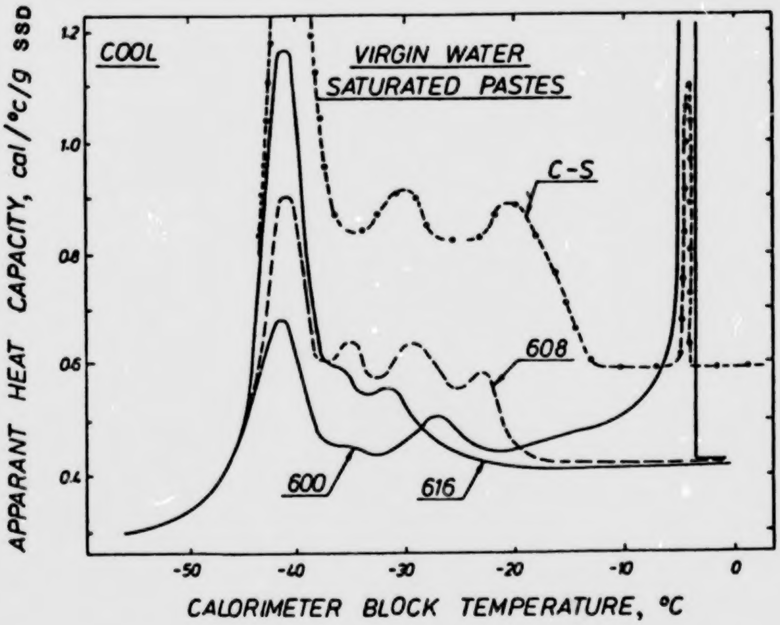

Fig. 6.2 — Low-temperature calorimetry (heat flow) for virgin, water-saturated cement paste samples. The last two digits in the identification numbers represent CSF content. All samples have W/C = 0.60. Areas under the peaks are heat of fusion; proportional to amount of ice formed (6).

Lehtonen (111) provides more information by presenting curves for water uptake versus time. For concretes with W/C + S = 0.45 and 0 and 10% CSF contents, the critical degree of saturation was not very different in spite of variations in air contents. However, the water suction behavior was quite different. The reference concrete quickly reached a plateau, whereas the CSF concrete showed a much more gradual water absorption. These results indicate major differences between CSF and reference concrete in their drying and wetting behavior which probably are important in practical conditions, but are usually not taken into account in normal frost and durability tests.

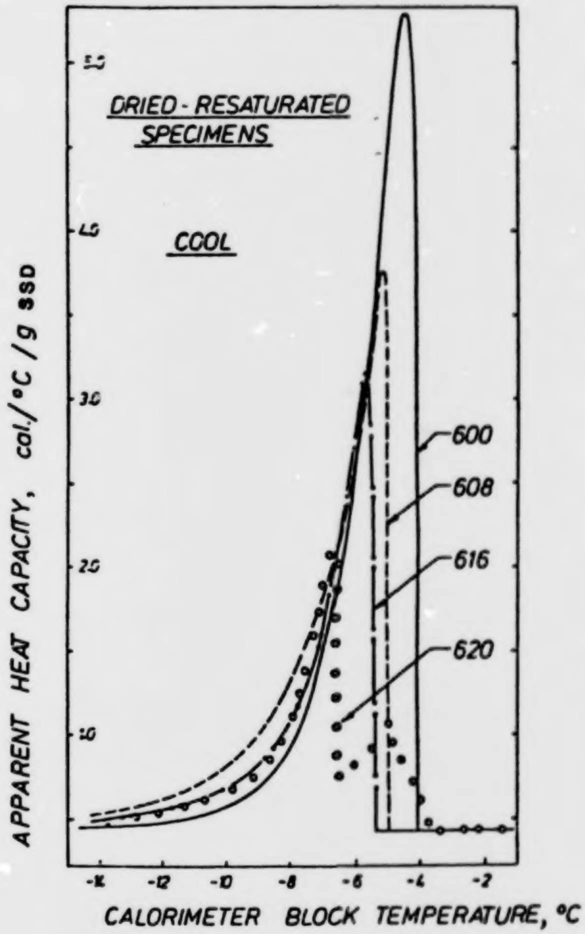

Fig. 6.3 — Low-temperature calorimetry (heat flow) for dried-resaturated cement paste samples. The last two digits in the indentification numbers represent CSF content. All samples have W/C = 0.60. Areas under the peaks are heat of fusion; proportional to amount of ice formed (6).

Frost-resistance testing

In the first paper published on CSF concrete in 1952, Bernhardt (121), included results on frost resistance. No admixtures were used, which resulted in an extremely high cement content (730 kg/m^3) to produce concrete of high slump and a water-to-cement ratio of 0.40. The CSF content varied from 10 to 30% and the water-to-cement ratio varied from 0.40 to 0.96. The test procedure consisted of freezing in air and thawing in sea water; frost resistance was assessed in terms of weight loss as a function of the frost cycles. Concretes with CSF performed significantly better than the controls, particularly for concretes well-cured prior to exposure to freezing and thawing. This observation agrees with later findings that CSF concrete requires more time to reach its potential.

Traetteberg (28) tested frost resistance of 15-day-old mortars with various air contents. The CSF content was from 0 to 25% and the W/C + S was in the range 0.48 to 0.83. The test procedure was freezing in air and thawing in water; damage was evaluated in terms of residual length change and decrease in dynamic E-modulus. All CSF mortars with W/C + S of 0.60 or less showed excellent frost resistance in terms of residual length change and dynamic E-modulus, whereas the controls required a ratio for water-to-cement of 0.40 to be resistant. However, strength tests done after exposure of both the control mortar and the one with 5% CSF (both with air-entraining and water-reducing admixture) showed practically zero bending strength. For the CSF mortar, this is in direct contrast to the other *indirect* measures of frost resistance. The observed contradiction between the direct and indirect measures of frost resistance for samples with water reducers and air-entraining admixtures was not consistent for other mixtures. Later work has not revealed any similar pattern, and hence, one must conclude that Traetteberg's results are anomalous. The main conclusions of the paper is that the use of CSF improves the frost resistance of mortars, and that the frost resistance is less dependent on a proper air-void system. Traetteberg also measured pore size distribution of the mortars by mercury intrusion and concluded that the positive effects of the CSF on frost resistance are related to alterations in the pore-structure.

Cheng-yi and Feldman (31, 122) also tested frost resistance according to ASTM C666 Procedure B, "Freezing in air and thawing in water" of mortars with W/C + S = 0.45 and 0.60, containing 0, 10, and 30% CSF. At the high W/C + S the addition of CSF improved the performance. At low W/C + S, the use of 10% CSF led to improved resistance, however 30% CSF resulted in poor frost resistance despite the greater strength of the mixture. None of the mortars were air-entrained. The good results for CSF mortars were attributed to an increase in the pore volume in the range 0.35 to 20 μm which they believe act as air pores because of their inkbottle shape. However, no data are given on the degree of saturation during the tests. They suggest that the observation showing that the strongest mix gave the lowest frost resistance is caused by a combination of low permeability and a higher CSF content than is needed for complete pozzolanic reaction.

As part of a comprehensive study the frost resistance of 25 concrete mixtures with and without CSF has been investigated, Opsahl (123). The method used was ASTM C666; in addition to the measurement of dynamic E-modulus, the compressive strength of the concretes after freezing and thawing treatment was determined. In an effort to provide an accelerated comparison between the concretes, none of them were air-entrained. The results showed that the efficiency factor of the CSF with respect to frost resistance is greater than with respect to compressive strength.

Carette and Malhotra (40) also tested the frost resistance (ASTM C666 Procedure A, "Freezing in water and thawing in water") of concrete containing 0 to 30% CSF, all having W/C + S = 0.40. Various additions of a superplasticizer were used to obtain workable concretes, and all concretes were air-entrained. The results were that the increasing CSF content led to decreased frost resistance, particularly for high CSF amounts. Air-void characteristics were determined for the concretes, but they do not explain these results. However, in terms of the general experience with CSF concrete, the compressive strength of the freezing and thawing series of concretes were anomalous in that cement replacement levels from 5 to 20% CSF gave almost identical 28-day strengths. Normally, increased replacement levels should lead to substantial strength increase. There is no obvious explanation for these differences.

Aitcin and Vezina (112) report on the freezing and thawing resistance of reference concrete and concrete where cement was replaced 3:1 by CSF. The test method used was ASTM C666 Procedure B, and the CSF content was about 8%. Both mixtures were air-entrained and the hardened concretes had the same average bubble-spacing factor. They concluded that the "CSF concrete was far superior to the plain concrete."

Yamato et al. (124) tested (ASTM C666 Procedure A) concretes with W/C + S of 0.25, 0.35, 0.45, and 0.55, and CSF contents of 0, 5, 10, 20, and 30%. Except for the highest W:C + S ratio none of the mixes were air-entrained. Freezing and thawing testing was initiated after 28 days of curing in water. None of the samples, including the air-entrained ones had satisfactory air-void systems. The test results showed that all concretes with W/C + S = 0.25 had durability factors above 90, decreasing somewhat with increasing CSF content. For higher W/C + S, none of the concretes performed satisfactorily, but the general trend was that the poorest performance was for those with 20 and 30% CSF content. This finding is in line with the results reported by Carette and Malhotra (40), and Cheng-yi and Feldman (31), which indicate that very high (20–30%) CSF content at W/C + S in the range 0.35 to 0.55 is detrimental to frost resistance, whereas lower contents generally appear to be beneficial over a wide range of W/C + S.

The resistance of CSF concrete to freezing and thawing treatment with deicing salts has been reported by Sørensen (125). The test was performed according to RILEM Recommendation CDC 2, on virgin specimens as well as on companion specimens pre-dried at 45°C for 14 days. The results showed that the pre-drying treatment had a detrimental effect, particularly on the control mixes.

Air-entrainment was in general very beneficial, but concrete containing 10% CSF with a W/C + S = 0.38 was resistant without any air-entrainment. However, concretes of equivalent composition have proved less frost resistant in later studies.

Lehtonen (110, 111) performed salt-scaling experiments on air-entrained concretes with 0 to 15% of the cement replaced by CSF. All concretes had W/C + S = 0.45. His results showed significant improvement to scaling with increasing CSF content. Beyond 28 cycles as recommended by the RILEM Standard, the trend for the CSF concrete was an increased rate of scaling. However, at 56 cycles, the scaling of all CSF concretes were well below that of the control concrete.

Virtanen (108) investigated the influence of CSF, fly ash, and slag replacement for cement on frost resistance. All mixes were both with and without air-entrainment, and were proportioned to give about equal compressive strength (30–40 MPa). Pore structure and air-void characteristics were determined, as well as parameters from frost-resistance and salt-scaling experiments. Virtanen concluded that the addition of CSF improves the freezing and thawing resistance of concrete compared with control concrete having the same strength and air content.

In a further series of experiments, Virtanen (109), focused on developing highly durable concrete for edge beams designed for road bridges. The mixtures were based on a cement content of about 400 kg/m^3 with 1:1 replacement of cement with CSF, and the CSF contents of 0, 4, 8, and 16%. Both superplasticizers and air-entraining agents were used. The 28-day compressive strengths were in the range of 42 to 56 MPa. The freezing and thawing testing consisted of alternately placing 100-mm cubes in water at 20°C (16 h) and then freezing in a salt solution at −15°C (8 h). The Finnish requirement states that the volume of the test specimens must not decrease by more than 5% after 25 cycles. The result, in all cases, was that the scaling was reduced with increasing CSF content, in spite of decreased air contents with increasing CSF content (Figs. 6.4 and 6.5).

Rasmussen (113) reports on a large, long-term, field-exposure test program on air-entrained concretes with several types of cement and varying CSF contents. The interim report is on laboratory salt-frost testing (similar to ISO 4846) on samples similar to those exposed in the field. The mixes were divided into three classes according to cement content, in CSF mixes 10% content was used and cement was replaced by CSF in a ratio of 3:1. The poorest performance was for mixes with blended cements (25% fly ash) and CSF (mixes with cement content 200 and 260 kg/m^3). This is probably because pre-curing was only 14 days in water, then 14 days in air; not enough time for the fly ash to develop its potential. The richer mixes (cement content 300–400 kg/m^3) all performed well.

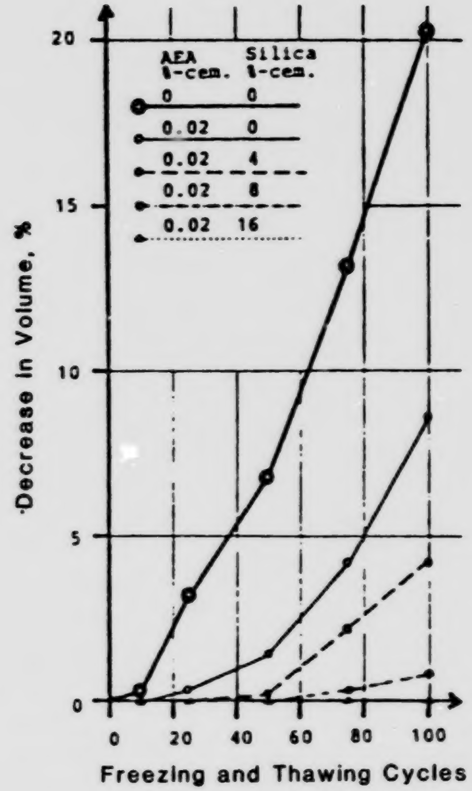

Fig. 6.4 — Volume decrease as a function of freeze–thaw cycles in salt-frost testing (109).

One disturbing aspect of the results is the lack of repeatability of the freeze–thaw testing. In a second test, much less scaling was recorded for all samples relative to the first, presumably identical, test. The internal ranking between the different mixes in the series was the same, however. This highlights the reproducibility problems associated with present standardized test methods, which can, in their present stage of development, apparently be expected to produce a ranking order among different samples tested at the same time. Testing against absolute criteria is obviously hazardous.

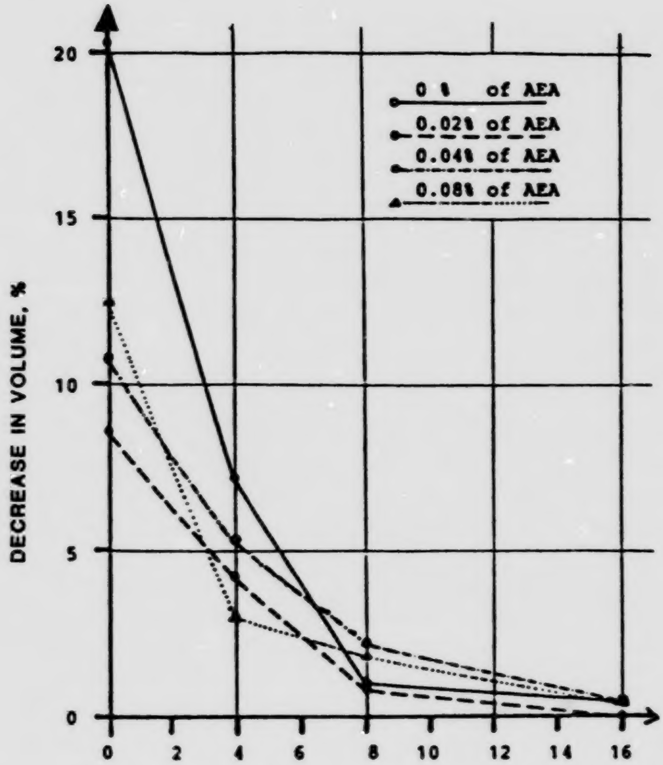

Fig. 6.5 — Volume decrease as a function of CSF content after 100 freeze–thaw cycles (109).

At the Technological Institute, Department of Building Technology, in Copenhagen, Denmark, investigations of drilled cores of CSF concrete from a number of structures have been part of a quality control program, (32). Several methods were used to assess frost resistance including a dilation method, equivalent to ASTM C671, and salt-scaling tests. They concluded that "CSF generally improves the frost durability of concrete as measured by frost resistance testing."

Conclusions: frost resistance

Frost resistance of CSF concrete has been investigated using a number of different methods. The results indicate that at contents of less than 15%, CSF increases the frost and salt-scaling resistance of concrete over the whole range of W/C more than it improves the compressive strength. At high CSF contents (20 to 30%), however, there is evidence indicating that the resistance is decreased in the low W/C (from 0.35 to 0.55).

Care must be taken in applying standard test methods to CSF concrete. Its drying and rewetting response may be much slower than for ordinary concrete. In addition, the response to the number of freezing and thawing cycles may be different, in that at a given low number of cycles (about 25) the deterioration may be marginal, but deterioration may accelerate later. It is therefore recommended that test specimens should be subjected to more cycles of freezing and thawing than normally prescribed. Long-term field data on the performance of CSF concrete are sparse, but the data available indicate no particular problems regarding frost resistance of CSF concrete.

Chemical Resistance

Leaching and efflorescence

Efflorescence frequently occurs on concrete surfaces exposed to wetting and drying or to percolation of water through the concrete. The main cause is leaching of calcium hydroxide which carbonates on the surface. Efflorescence is mainly an esthetic problem, but, if extensive leaching of lime takes place in the concrete, the porosity is increased with decreased strength and durability as a result.

Samuelsson (126) measured the leaching of lime from mortar surfaces with 0, 5, and 10% CSF additions at a fixed ratio of water-to-cement; different pre-curing times and relative humidities were considered. He concluded that the most efficient preventive measure was to pre-cure the concrete at 80 to 95% RH for several days prior to the exposure to leaching water. This allows hydration to proceed and carbonation to take place in the pore system. The effect of the CSF was to reduce leaching, provided the pre-curing period was at least four days in a moist atmosphere. Curing periods beyond four days were not investigated. One might expect more effect from CSF addition if time is allowed for the pozzolanic reaction to go further, thereby reducing the free lime content and providing a finer pore structure.

For concrete submerged in water, the leaching of lime is a major weakening factor. Carlsen and Vennesland (127) made cement pastes with sulphate-resistant and rapid-hardening portland cements, and with 0, 5, and 10% CSF. The W/C + S was kept constant at 0.50. Mature 12.7-mm cube specimens were exposed to sea water for 540 days. All specimens showed strength reductions of about 50%. The authors give no explanation for this surprising result.

Sulphate resistance

The first published report on CSF in concrete in 1952 (121), contains data on sulphate resistance of concrete stored in a 10% sodium sulphate solution. Bernhardt concluded that the sulphate resistance was improved when 10 to 15% of the cement was replaced by the CSF, but he stressed that the duration of the tests was too short to allow firm conclusions to be drawn.

In 1952 a large number of concrete specimens were placed in a tunnel in Oslo's alum shale region for long-term tests. The ground water contains up to 4 grams of SO_3 per litre and the pH varies from neutral to 2.5. Two reports have been published so far, Fiskaa et al. (128) on 12-year results, and Fiskaa (129) on 20-year results. The test specimens were produced with a variety of cements and additives, including one set where 15% of ordinary portland cement was replaced by the CSF. All mixtures had a water-to-cement ratio of about 0.50, except for the CSF mix which had a higher water demand, and therefore $W/C+S$ of 0.62. Damage was assessed by measuring volume reductions. After 20 years of exposure the most resistant concretes were those with sulphate-resistant cements and the CSF concrete, which all performed about equally well (Fig. 6.6). The reasons for the good performance of the CSF concrete include:

— the refined pore structure and, therefore, a reduced transport rate of harmful ions (26);

— a lower content of calcium hydroxide;

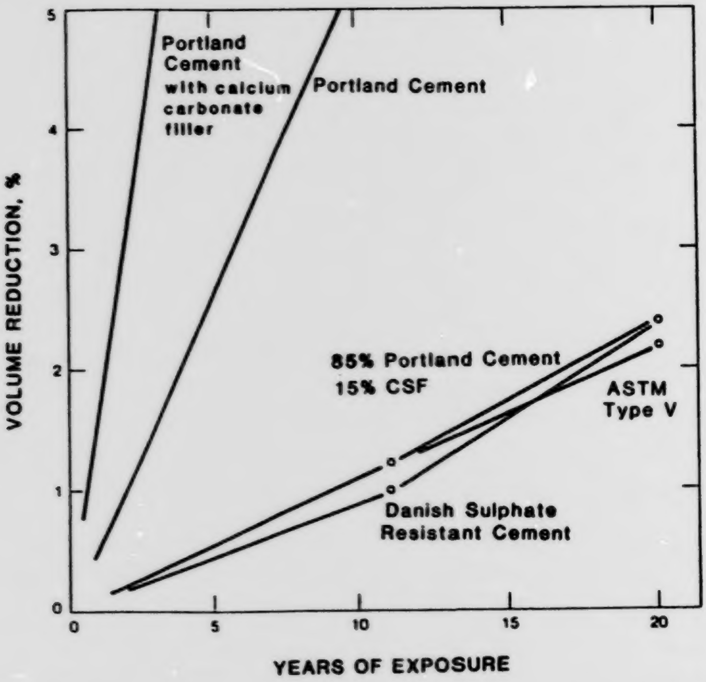

Fig. 6.6 — Volume reduction of 100 x 100 x 400-mm concrete prisms stored for 20 years in acidic, sulphate-rich water in Oslo alum-shale region (1, adapted from 129).

- an increased amount of aluminium incorporated in the CSF products, thus reducing the amount of alumina available for ettringite production (1).

Inspection of the test samples after 30 years of exposure confirm the results cited here (130).

Laboratory investigations confirm the data from the field tests. Mather (131) measured expansion in a sulphate solution of mortar prisms where 30% of the cement was replaced by an equal volume of various pozzolans. Three types of cements were used, and the CSF in combination with all the three cements proved the most efficient binder system in preventing expansion.

Carlsen and Vennesland (127) measured strength reductions of cement pastes after exposure to a sodium sulphate solution. They found good performance for a paste made with sulphate-resistant cement and one made with rapid-hardening portland cement containing 5% CSF, whereas the control with rapid-hardening portland cement was destroyed quite quickly.

Popovic et al. (132) used OPC, a blended cement with 20% slag, and a blended cement with 15% natural pozzolan to produce control mortars and mortars to which 15% CSF was added alone, and together with a superplasticizer to compensate for the increased water demand in the CSF mixtures. After 28 days of water-curing the small prisms (25 x 25 x 160 mm) were exposed to a 10% ammonium sulphate solution. They concluded that sulphate corrosion is predominant in this solution, and that CSF prevents this type of corrosion as well as acid corrosion. The Steinegger–Koch test in sodium sulphate solution "confirmed this conclusion completely, and the fact that ordinary and blended portland cement with admixture of silica fume exhibit better durability than special sulphate resisting cement." It is interesting to note that in these results CSF was equally as effective with and without superplasticizers, i.e., at different total porosities. The CSF inhibits ammonium sulphate corrosion, which implies that the chemical effect of CSF is more important than reduced permeability in this connection.

Mehta (133) compared the resistance to chemical aggression of concrete with OPC, latex-modified concrete, and concrete containing 15% CSF. The W/C + S of the three concretes was about 0.33. Curing was in air for the latex concrete, the two others were wet-cured for seven days. After one week all concretes were air-cured for six weeks prior to exposure to the aggressive media. Two sulphate solutions were used; 5% ammonium sulphate and 5% sodium sulphate. The failure criteria was the amount of time samples needed to suffer a 25% weight loss. Ammonium sulphate was equally destructive to the control and to the CSF concrete, whereas the latex concrete suffered less weight loss. Mehta attributes this to the ability of ammonium sulphate to decompose CSH, while the latex coating delays the decomposition. Note that this result is in contrast to the one by Popovic et al. (132), in which the CSF concrete performed better than the control concrete in a more concentrated solution. None of the three concretes (133) decomposed in the sodium sulphate solution, a result Mehta attributed to the low water-to-cement ratio.

Alkali–aggregate reactions

It is well known that reactive pozzolans can be used to control the expansions associated with the alkali–aggregate reaction. Pore water analysis of the CSF–cement paste (21 and 22) demonstrated the ability of the CSF to reduce the alkali concentrations in the pore water quite rapidly, thus making it unavailable for the slower reaction with reactive silica in the aggregates.

Asgeirsson and Gudmundsson (134) used CSF with high-alkali Icelandic cements and reactive sands in mortar bar tests and demonstrated the ability of the CSF to reduce expansions (Fig. 6.7). Olafsson (135) reports further Icelandic experiences on blended cements made with the CSF. The presence

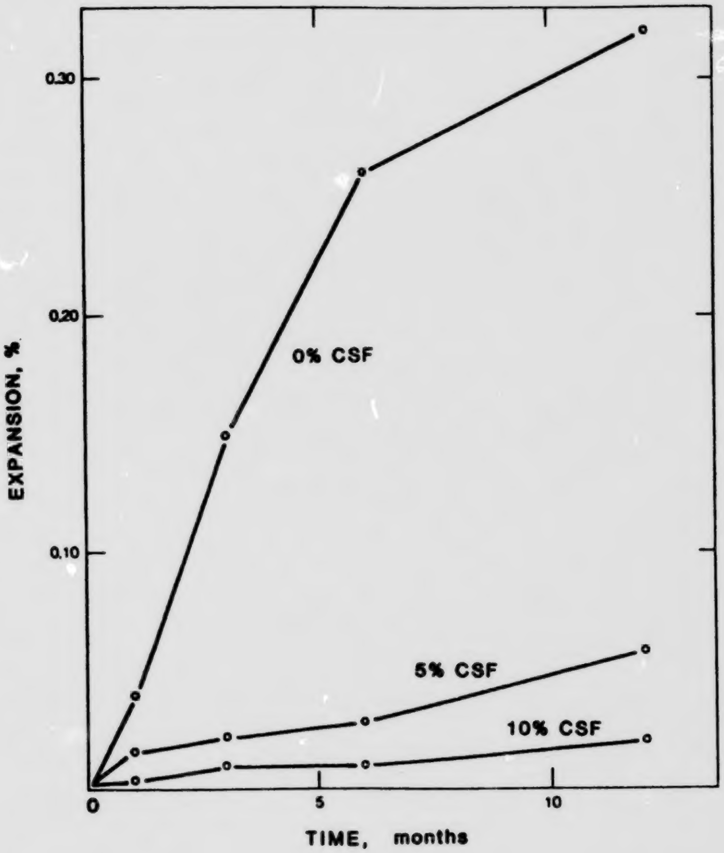

Fig. 6.7 — Expansion of mortar prisms made with high-alkali cement, reactive sand, and three CSF contents (1, based on data from 134).

of salts (from sea-dredged aggregate) was generally found to increase the alkali–aggregate expansions. The CSF contents of 5 and 15% were found to reduce the expansions, both with and without the presence of salts. A characteristic of the expansions in these specimens containing CSF was that it takes place over a long period. Short-term tests (14 days) are, therefore, not suitable to evaluate the effect of the CSF. Expansions were found to decrease with decreasing lime-to-silica ratios in the blended cements. This observation has been used to determine the necessary CSF content to prevent harmful expansions. At present, all Icelandic cements are blends containing 7.5% CSF. No report on the field experience in Iceland is available yet.

Oberholster and Westra (136) tested a number of mineral admixtures for their efficiency in reducing alkali–aggregate expansions in mortars containing high-alkali cements. CSF was found to be the most efficient. The reactivity of several Scandinavian sands was tested by means of various methods in a Nordtest project (137). The prime purpose of the work was to compare the test methods; however, a number of mortars clearly demonstrated the ability of CSF to reduce expansions.

Perry and Gillott (138) measured mortar bar expansions at 23, 38, and 51°C by using a pessimum amount of reactive opal aggregate and blended cements. They found that the CSF reduced the total expansions considerably, but also found, as did Olafsson (135), that the expansions were delayed for the CSF mortars. The 5% CSF content increased the expansion, and they concluded that probably as high as 20% of the cement needs to be replaced by CSF to effectively suppress the expansion with their very reactive aggregates. A noteworthy aspect of their work was the discovery that the use of a superplasticizer dramatically increased expansions relative to the control mortars without the superplasticizer. This was particularly evident for the CSF mortars, and could not be explained by the alkalis contributed by the superplasticizer. They also concluded that the CSF was inefficient in supressing expansion resulting from the alkali–carbonate reaction, although some reduction was observed.

Nilsson and Petersson (139) studied the relationship between the moisture state and the *pop-outs* caused by alkali–silica reactions. The use of the CSF as an inhibitor was also tested, and was found efficient in preventing pop-outs at a 5% CSF content level. The 10 or 15% CSF content was needed to prevent expansions.

The CSF from two different sources was used in both investigations by Perry and Gillott (138) and Nilsson and Petersson (139). In both cases, one source proved significantly more effective than the other.

The ability of the CSF as an inhibitor against pop-outs was also investigated by Petersson (140). He was unable to draw any firm conclusions from his results regarding the pop-outs, but found that fine aggregates could not be protected by as much as 10% CSF content.

The already cited investigation by Popovic et al. (132) also included the efficiency of CSF in preventing alkali–silica expansion in concrete. By using 23% CSF content by weight of a cement containing 0.8% total alkalis and Pyrex glass aggregate (ASTM C441), no expansion was observed.

Aitcin and Regourd (141) report on a field test follow-up after three years on a series of concretes with very reactive aggregates and alkali-rich cement. Lean concretes with high CSF contents (20 to 40%) showed no traces of gel formation, whereas traces were found in richer concretes containing 15% CSF. The alkali–aggregate reaction was considered to be under control in all concretes.

Other chemicals

Improved resistance of concrete to a large number of chemically aggressive agents including nitrates, chlorides, sulphates, and acids have been reported by using a proprietary product which contains 80% CSF (142).

Popovic et al. (132) found that 15% CSF was efficient in *preventing* corrosion of OPC mortars in 5% sulphuric acid solution and 5% ammonium nitrate fertilizer solution. *Preventing* in this connection means strength decrease relative to a control exposed to the same aggressive agents — not relative to a control in water. The CSF also greatly improved the resistance to a 10% ammonium nitrate solution. The performance of the CSF with OPC, a 20% slag blend, and a 15% natural pozzolan blend was both comparable and reproducible.

Mehta (133) compared the response of a control concrete, a latex-modified concrete, and a 15% CSF concrete on exposure to 1% hydrochloric acid solution, 5% acetic acid solution, 1% lactic acid solution, and 1% sulphuric acid solution, respectively. All concretes had a water-to-cement ratio of about 0.33. The results showed that the CSF concrete generally had the best resistance to the chemical attack.

Feldman and Cheng-yi (143) measured the resistance of mortars to a 4% $MgCl_2$ solution for 150–170 days followed by exposure to a mixed chloride solution of 27.5% $CaCl_2$, 3.9% $MgCl_2$, 1.2% NaCl, and 2.1% $NaHCO_3$. The mortars had W/C + S of 0.45 and 0.60 with 0, 10, and 30% contents of CSF. Curing times before exposure were 7 and 28 days. The investigation included measurements of mercury intrusion, stiffness, calcium hydroxide contents, and non-evaporable water contents before and after exposure. They concluded that the CSF and long curing time prior to exposure substantially increased the resistance of the mortars. They attributed this effect mainly to inherent lowered permeability, but also to the reactions between excess CSF, low-calcium CSH, unhydrated cement, and the salt solution, which results in reduced total pore volume and, thereby, in reduced permeability.

Conclusions: chemical resistance

Many investigations as well as practical experience have indicated that a major potential advantage of CSF in concrete is to improve its chemical resistance.

Sulphate resistance and protection against alkali–aggregate reactions are two areas that show particular promise. Recent reports indicate that the same is true for a variety of chemically aggressive substances.

The reasons for the generally good performance of CSF concrete in chemically aggressive environments include:

- refined pore structure, and therefore reduced transfer rates of harmful ions;
- reduced content of calcium hydroxide;
- lower C/S of the reaction products, which increases the capacity to incorporate foreign ions such as aluminium or alkalis in the lattice.

7. CORROSION OF REINFORCEMENT

The corrosion process of reinforcement steel in concrete may be divided into two stages; the initiation stage and the propagation stage. Steel in concrete is normally in a passive state with respect to corrosion, because of the high pH value in the pore water. The passive iron oxide layer that normally protects the steel is destroyed either when the pH value is reduced below about 10 to 11, or when chloride ions reach the steel surface even at higher pH values. The rate of corrosion, once the passive iron oxide layer is destroyed, depends on the presence of moisture and oxygen, and on the electrical resistivity of the concrete.

pH Values: Pozzolanic Reaction and Carbonation

Scandinavian cements have relatively high alkali content which results in high pH values for concrete pore water (>13.5). The CSF reduces the alkali content of the pore water much more than the *dilution* effect when it partly replaces cement on a 1:1 basis. Page and Vennesland (22) found pH values of pore water in mature pastes to be about 13.9, 13.4, 12.9, and 12.0 for 0, 10, 20, and 30% cement replacement levels, respectively (Fig. 7.1). Thus, 30% replacement of cement by CSF is needed before the pH value drops below the approximate pH value of 12.5 of a saturated, calcium hydroxide solution.

Diamond (21) determined a pH value of 12.2 after 145 days hydration for a paste with 30% of the cement replaced by CSF. In a later work Diamond (144) reports pore water analysis made 4 and 24 hours after mixing of an equivalent paste as well as a reference. There are some changes not caused by the dilution effects, but the main conclusion is that CSF has "little measureable effect on the major dissolved component species" during the first 24 hours. More time is obviously needed for producing the effects observed after long periods.

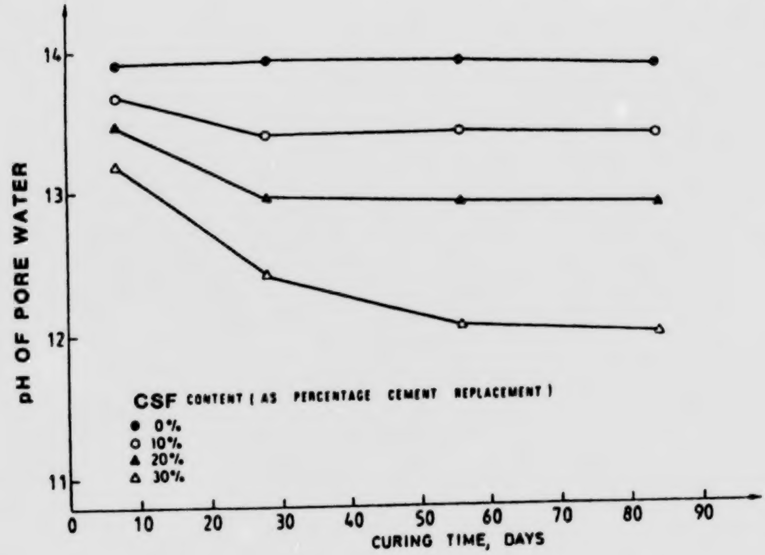

Fig. 7.1 — Influence of CSF content on pH values of pore water squeezed from cement pastes. Ordinary portland cement, W/C+S = 0.50 (22).

Glasser and Marr (145) mixed mortars with a low- and a high-alkali cement (W/C = 0.60) as well as blends where 15% of the cements were replaced by the CSF. Pore water was squeezed out and was analysed. The pH stabilized after three months and for the high-alkali cement the values were 13.77 for the reference mortar and 13.18 for the CSF mortar, in line with earlier results by Diamond (21). The calcium hydroxide content was reduced by more than one-half. CSF had much more effect than any of the fly ashes or natural pozzolan tested, but the reactivity with calcium hydroxide was comparable to a Degussa flame hydrolysis silica. The CSF reduced the alkali contents to roughly one-third relative to the control OPC, the soluble sulphate was also markedly reduced to less than one-half, but the chloride concentration was increased somewhat in contrast to all the other mineral additives. The authors state that it is the low C/S of the CSH formed in the presence of CSF which is responsible for the alkali depletion, either by sorption, or by stabilizing alkali-rich compounds.

Gautefall and Vennesland (146) report analysis of pore water for cement pastes made with OPC, fly ash blends (10 and 25%), and a granulated slag blend (15%), all with 0 to 15% CSF. The results regarding the ability of CSF to reduce pH values and alkali pore-water concentrations are in general agreement with results already cited, although the values of the reductions depend somewhat on the type of cement.

The results cited here for high contents of CSF are consistent with thermogravimetric data which indicate that more than 24% CSF by weight of cement is needed to consume all the calcium hydroxide (6).

The CSF does reduce the pH of concrete pore water for all cement types, but at normal CSF content the reduction is far from sufficient to destroy the passivity of the steel.

When concrete carbonates, the pH is reduced enough to depassivate the steel. Carbonation takes place both at the expense of the calcium hydroxide and of the CaO in the CSH phase. The fact that CSF concrete contains less calcium hydroxide than control concrete does not necessarily mean that CSF concrete is more vulnerable to carbonation. Other factors also influence the rate of carbonation; curing history, moisture state, and CO_2 diffusion rates. Because of the complexity of the problem it is considered that direct measures of carbonation depths are more relevant than theoretical predictions based, for example, on the amounts of calcium hydroxide.

Meland and Traetteberg (147) measured calcium hydroxide and calcium carbonate contents in 3- to 4-mm-thick cement paste discs with $W/C + S = 0.50$ and with 0 and 15% of the cement replaced by CSF, after various durations of exposure to air of 50 and 100% RH with 1 and 3% CO_2 content. The CSF paste was moist-cured for 21 days prior to exposure, and the control paste was moist-cured for 7 days. The calcium hydroxide contents of the uncarbonated pastes agreed reasonably well with data from Sellevold et al. (6), taking into account the different cements used. However, other results were of a novel nature. In line with common experience, the control paste carbonated most at 50% RH, but the CSF paste carbonated much more at 100% RH than at 50% RH. Also, in the time range from one to six months substantial carbonation took place in the CSF paste, but the calcium hydroxide content hardly changed. A similar tendency was found for the control paste. It should be noted that the CO_2 pressure was much higher than under natural conditions in these tests. No firm conclusions can be drawn from these experiments, but they certainly point out the need for more knowledge about the carbonation phenomenon, and about the influence of reactive pozzolans on the cement hydration and on the hydration products.

Carbonation of concrete is usually measured by the phenolphthalein test on fracture surfaces perpendicular to the surface exposed to carbonation. Johansen (50), Vennesland and Gjørv (98) and Vennesland (148) made carbonation measurements up to three years on a large number of concrete specimens with and without CSF. Vennesland's results showed that when carbonation depth was plotted versus the 28-day compressive strength of water-cured specimens the 10% CSF content had no influence on the carbonation depth for specimens cured for seven days in water prior to exposure to laboratory air. Johansen (50) exposed the specimens directly upon demoulding. His results after three years show two clear effects:

— Lack of moist-curing at least doubles the carbonation depth for both types of concrete.

- CSF concrete is even more sensitive to lack of proper curing than normal concrete.

Thus, as is well known, proper curing of concrete is essential to avoid excessive carbonation.

Johansen (149) measured carbonation depths on the same concretes after six years of exposure, both for the specimens exposed directly to carbonation after demoulding, and after 27 days of water-curing (Fig. 7.2). Inadequate curing still has a major effect on carbonation depths; for concretes with strength >40 MPa at 28 days, the carbonation depths were approximately doubled relative to the

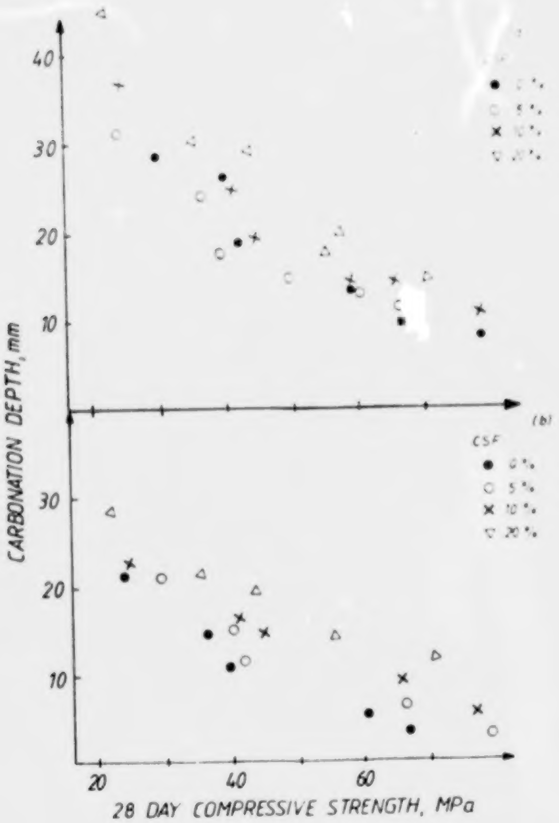

Fig. 7.2 — Carbonation depths of concretes after six years of exposure at 20°C and 50% RH. Pre-curing prior to exposure: (a) one day in mould, (b) one day in mould, then 27 days in water (149).

water-cured companions. The factor was smaller for low-strength concretes, but the carbonation depths were of course greater. For example, poorly cured control concrete (25 MPa) showed a carbonation depth of about 32 mm, whereas a well-cured companion showed about 22 mm. The effect of CSF (5, 10, and 20% contents) was small at 5% content, but the trend was clear for both types of exposure when comparison was made on an equal 28-day strength basis — increased CSF content led to increased carbonation depths.

To obtain data from a variety of field conditions Maage and Sellevold (150) took samples from 16 buildings with CSF concrete and 11 buildings without CSF concrete. The age of the buildings varied from 40 to 80 months, and the concrete in all cases had a nominal characteristic strength of 25 MPa. The measured carbonation depths were adjusted to correspond to an age of five years. The results showed that there was no significant difference between the mean values for carbonation depth for the two types of concrete (9–10 mm). The CSF concrete, however, showed much greater variation in carbonation depth than the control concrete. It seems likely that this reflects the greater sensitivity of CSF concrete to early curing conditions, which certainly varies considerably between building sites.

The CSF concrete of higher quality from structures has also been investigated. Christensen (32) found no influence of CSF on carbonation depth. Drilled cores from a pier in Gothenburg, Sweden, have been investigated by Maage (102). None of the five concretes (three with CSF), with drilled core strengths from 44 to 68 MPa, showed carbonation depths of more than 2 mm after about seven years of service. The same was true for the two 12-year old concretes, one with CSF (60 MPa strength) and one control (50 MPa strength), from a silo cover at Fiskaa Works, Kristiansand, Norway.

Carbonation of concrete in the Middle East for a variety of curing and exposure conditions has been reported by de Fontenay (151). Some concretes with 5% CSF were also included in this study. He concluded that CSF added to improve durability has no influence on the rate of carbonation.

Based on the foregoing, it seems that the use of CSF will increase carbonation at content levels of more than 5% in poorly cured, medium- to low-strength concrete. There is no field evidence indicating that carbonation is a problem in high-quality concrete, either with or without CSF. Laboratory tests up to six years indicate that for equal strength, CSF concrete will carbonate somewhat more than the control concrete regardless of strength class or exposure condition.

Chlorides

Chlorides either may be introduced into fresh concrete from chemical admixtures or from chloride contaminates, or they may penetrate hardened concrete from external sources (such as deicing salts and sea water). In either case, only some of the chloride ions will be available, and presumably aggressive, in the pore-water solution. The capacity of a concrete to bind chlorides is, therefore, of interest, as well as the resistance it offers to the penetration of chlorides.

Page and Vennesland (22) added chlorides to cement–CSF pastes, and later squeezed out pore-water for analysis. Their results showed that as the CSF content increased, the fraction of the chlorides available in the pore water also increased. They suggested this effect to be caused by the lowered pH value, which increases the solubility and thereby reduces the quantity of Friedel's salt. Friedel's salt, a calcium chloro-aluminate hydrate, is thought to be the dominant factor in binding chloride ions during cement hydration. The lower pH of the CSF concrete also indicates that the threshold concentration of chlorides in the pore water, which will induce steel depassivation, is reduced.

The hypothesis that there is a critical ratio of chloride to hydroxyl concentrations in concrete pore water with respect to inducing depassivation of steel, was followed up in further work by Page and Havdahl (152), by electrochemical monitoring of the corrosion behavior of steel electrodes in CSF–cement pastes of similar compositions to those studied earlier (22). They concluded that the free chloride:hydroxyl ratio alone was not a reliable index for comparing the corrosiveness of hardened pastes with varying CSF contents. Passivity returned in some pastes after some initial corrosion had occurred, presumably because of insufficient mobility of chloride ions in the dense pore structure of CSF–cement paste. Thus the results at present indicate that acceptable chloride limits are lower for CSF concrete than for reference OPC concrete, but further work is required on exposure for longer periods together with data on chloride diffusion (152).

Monteiro et al. (153) studied the steel–cement paste interface for a reference mixture, and for one in which 16% of the cement had been replaced by CSF. Calcium chloride was added at a rate of 2% to the fresh concrete. After storage in a fog room for 180 days, the pastes were dried, which led to the separation of the steel from the matrix. The interfacial zone was examined by the scanning electron microscope. Both pastes showed an interfacial film of large, calcium hydroxide crystals, but only the CSF paste showed visual evidence of corrosion. The authors attribute this result to a higher chloride:hydroxyl ratio in the pore water for the CSF paste. However, in light of the work by Page and Havdal (152) already discussed, it is not known whether passivity had been restored. Note that the chloride amount was twice as high in this investigation as that reported by Page and Havdal.

Penetration into CSF concrete of chlorides from sea water has been studied by Fisher et al. (154). With CSF used as an additive, they found that it reduced the diffusion coefficient of the chlorides in concrete considerably. For example, a concrete with 8% CSF addition had a chloride diffusion coefficient of 1.1×10^{-8} cm^2/s whereas an equivalent concrete without CSF had a coefficient of 1.5×10^{-7} cm^2/s.

Chloride penetration in concrete has been measured with somewhat inconclusive results by Vennesland (148). Penetration from sea water into the pastes was found by Gautefall (155) to decrease markedly when 5 to 15% of the cement was replaced by CSF (Fig. 7.3).

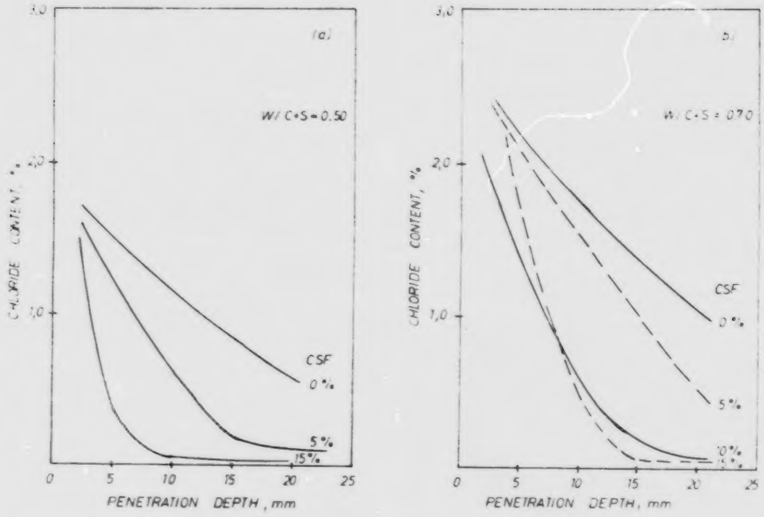

Fig. 7.3 — Chloride penetration into hardened cement paste. Specimens exposed to sea water for six months. Ordinary portland cement with W/C+S = 0.50 and 0.70. CSF contents from 0 to 15%. Chloride content is given as % by weight of the paste (155).

The diffusion of chlorides through discs of hardened cement pastes has also been measured by Gautefall (156). The W/C + S of 0.50, 0.70, and 0.90 were used with the CSF contents of 5, 10, and 15%. The OPC and a blended cement with 10% fly ash were used. The diffusion coefficient for the blended cement pastes were 30–50% lower than that for the OPC pastes. The replacement of cement by CSF led to marked reductions in the diffusion coefficient, particularly for the OPC pastes. For example, the use of 10% CSF led to reductions of from 68 to 84% in the OPC pastes.

For concrete bridge decks, the U.S. Federal Highway Administration has described a rapid chloride-permeability test. Christensen et al. (157) applied the test to compare a high-strength CSF concrete with a latex-modified concrete and with a low-slump dense concrete. The CSF concrete obtained a *very low* permeability rating, whereas the two other concretes were rated as *moderate*.

Rate of Corrosion

Vennesland and Gjørv (98) and Vennesland (148) measured oxygen diffusion and electrical resistivity of concretes with and without CSF. The oxygen diffusion did not show any systematic dependence on the content of CSF or water-reducing admixtures for water-saturated specimens.

The electrical resistivity of CSF concretes increased significantly to exceed resistivity of the control concrete presumably because of the lower ion concentrations and the refined pore structure.

Electrical resistivity of dry- and wet-cured concretes made with four cement types and CSF contents from 0 to 15%, has been reported by Gautefall and Vennesland (146). The dry-cured samples had high resistance and, thus, no corrosion due to the macrocell effects was possible. Wet-cured concrete generally showed only small decreases in resistivity with increasing W/C + S for a given cement type and CSF content. The use of CSF produced a substantial increase in resistance for all cement types (Fig. 7.4).

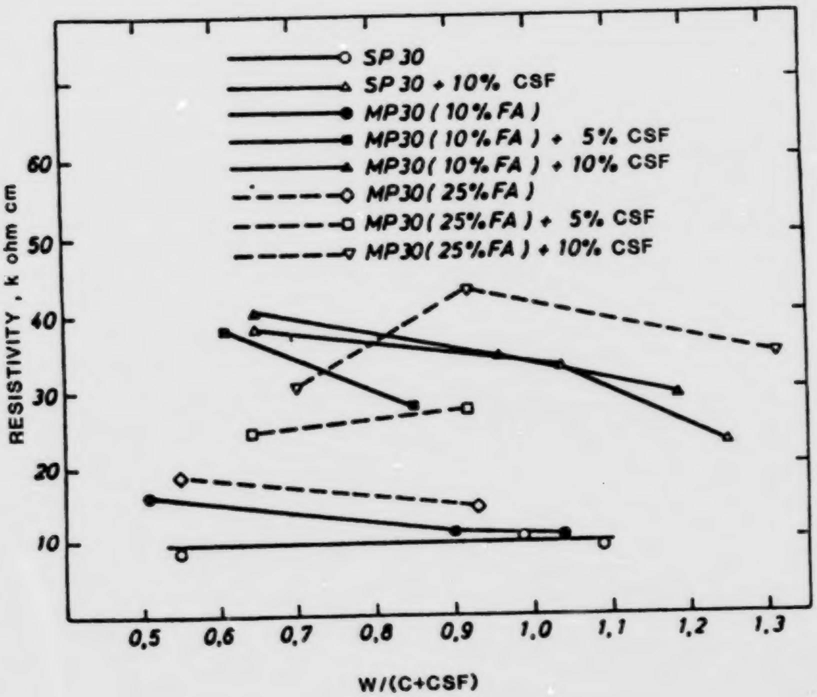

Fig. 7.4 — Electrical resistivity of concrete with different cement types, W/C + S, and CSF contents. Mature, water-cured specimens (146).

Fisher et al. (154) measured rates of corrosion in control concrete and in concrete with CSF addition. They found that the corrosion rate was about the same in the two concretes for equal total chloride concentrations. They also found the resistivity of the concrete to be considerably increased upon addition of the CSF.

Preece et al. (158) studied the electrochemical behavior of steel in dense CSF–cement mortars. They found that the mortar provided a high degree of corrosion protection to the steel, and attributed this to:

- low W/C + S resulting in a fine pore structure which apparently limits the access of water;
- high electrical resistivity, which limits the galvanic current even in the absence of passivity of the steel.

Bürge (159) has reported that the use of a dense polymer-modified CSF–cementing mortar incorporating corrosion inhibitors is very effective as a protective coating of steel in corrosive environments.

Cracks in concrete may result in the formation of concentrated anodic areas at the exposed steel, and consequently, in high corrosion rates. The ability of concrete to *self heal* is important in avoiding the corrosion problem. Gautefall and Vennesland (160) investigated the self-healing capacity of concretes with and without the CSF in sea water with access to oxygen, simulating a splash-zone situation. They found no significant difference between the two types of concrete.

Conclusions: Corrosion

As already discussed, the individual factors controlling the corrosion of steel in concrete are known and may be investigated. However, in practical situations it is the combination of these factors which govern the risk of corrosion, and information on the individual factors is insufficient to allow a direct prediction of the corrosion protection offered by different concretes. The present evidence suggests that the use of CSF as an *addition* to improve concrete durability will also improve its ability to protect embedded steel from corrosion. On the other hand, the use of the CSF to obtain maximum cement savings in low- to medium-strength concretes may result in a shortened initiation stage, and thereby increase the risk of corrosion.

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CHAPTER 4

THE REACTIVITY AND HYDRATION PRODUCTS OF BLAST-FURNACE SLAG

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1. INTRODUCTION

The purpose of this section is to provide some background on the reactivity of quenched-iron, blast-furnace slag. Prior to 1975 there was no significant use of slag as a cementing material in North America. Since then, large cement operations using separately ground slag began in Canada in 1976, in the USA in 1982, and further production at other locations is anticipated in both countries. As well, CSA and ASTM standard specifications have been developed for the use of separately ground slag.

First, the production and processing (including use) of blast-furnace slag are discussed in general. Then the relatively new development of pelletized slag is discussed in more detail because it is, until late 1986, the only type of slag available as a cementing material in Canada. Next, the cementitious aspects of slag and factors affecting its reactivity are dealt with. Lastly, the reactions of slag cements under autoclave-curing with various activators are covered.

2. IRON BLAST-FURNACE SLAG*

Production and Processing

The iron blast-furnace operation is a continuous process. The blended raw materials (burden) and coke are introduced at the top and as the materials move down through the furnace, they are heated from below. Air is injected near the bottom of the furnace and the ignited coke eventually supplies enough heat to melt the burden. The slag results from fusion of the fluxing stone (limestone or dolomite) together with the gangue (siliceous and aluminous residues from the iron ore) and coke ash in the blast furnace. (It should be noted that steel-making slag is typically recycled as part of the burden.) The molten slag floats on top of the molten iron and below the unmelted burden. Both molten materials are drawn off at regular intervals from the continuous-process furnace. Slag is tapped from modern blast furnaces using high-quality ore burdens at a rate of 280–340 kg per metric ton of hot metal (1). A flow chart for the production of blast-furnace slag is given in Figure 2.1. Because the raw-material burden is carefully controlled to give consistent iron production, the range of slag chemical compositions is fairly narrow for a specific ore and furnace operation.

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*Although there are many types of ferrous and non-ferrous slags, for brevity in this chapter, iron blast-furnace slag will be referred to as slag.

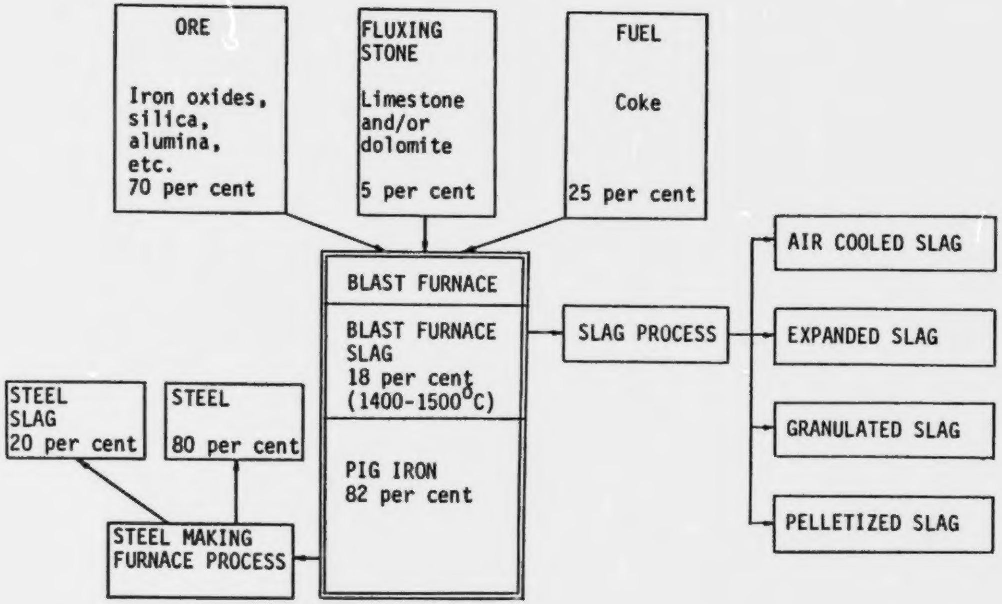
ORE
Iron oxides, silica, alumina, etc.
70 per cent
FLUXING STONE
Limestone and/or dolomite
5 per cent
FUEL
Coke
25 per cent
BLAST FURNACE
BLAST FURNACE SLAG
18 per cent
(1400-1500°C)
PIG IRON
82 per cent
SLAG PROCESS
AIR COOLED SLAG
EXPANDED SLAG
GRANULATED SLAG
PELLETIZED SLAG
STEEL MAKING FURNACE PROCESS
STEEL
80 per cent
STEEL SLAG
20 per cent

Fig. 2.1 — Flow chart of iron production and blast-furnace slag processes (75)
(Mass percentages shown are approximate)

The major oxides in the slag are not free but combined, and the equilibrium compositions of Canadian slags are typically mostly melilite solid solutions (between akermanite (C_2MS_2)* and gehlinite (C_2AS)) with minor amounts of diopside or monticellite. The range of blast-furnace slag compositions containing 10% MgO (typical of North American slags) is shown in Figure 2.2. Detailed studies on the compositions of blast-furnace slags and the influence of blast-furnace operations have been summarized by Osborn et al. (2), Kramer (3), and Schröder (1).

The physical state of the slag is fundamental to its cementitious properties. Until recently common North American practice was to cool the slag slowly in pits (referred to as air-cooled slag) which allows sufficient time for the molecules to arrange themselves into crystalline mineral compounds as the slag solidifies. Unfortunately, these crystalline compounds have little or no cementitious value (4). However, when quickly cooled or quenched from its molten state (after discharge from the furnace) the molecules in the slag are not given sufficient time to crystallize as high viscosity develops with falling temperatures. As a result, the disorganized liquid structure is retained in a metastable amorphous, vitreous, or glassy state**. The glass structure represents energy locked in the slag at a perched Arrhenius potential (5), and imparts latent hydraulic properties as discussed later.

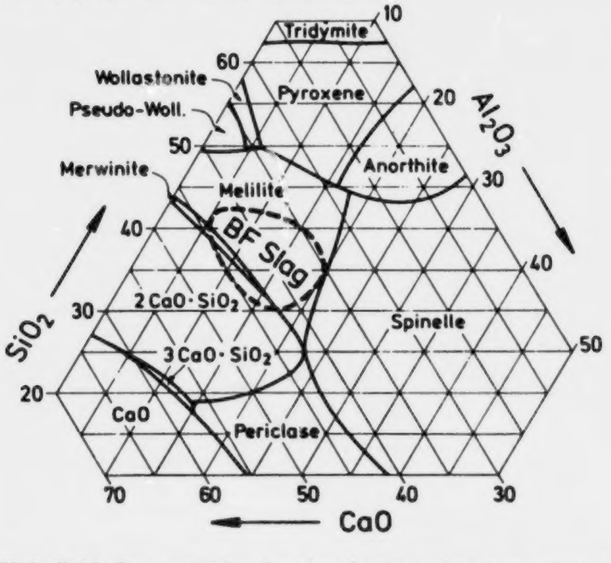

Fig. 2.2 — Main field of composition for blast-furnace slags containing 10% mass MgO (26)

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*Cement chemical notation: C = CaO, M = MgO, S = SiO_2, A = Al_2O_3, H = H_2O.

**The terms amorphous, vitreous, and glassy are used interchangeably throughout this chapter to describe the disorganized structure of quenched slag. The term commonly used by producers and users is glass.

Air-Cooled Slag

As mentioned previously, the bulk of available slag in North America was, and still is, cooled slowly in pits, and then is broken up and crushed for use as aggregate or granular base. However, since energy savings have become a more important consideration in the manufacture of cements, the production of hydraulically inert, air-cooled slag has decreased. Although perhaps not always used to its optimum "energy" advantage, it should be noted that blast-furnace slag is almost fully used and therefore must be classified as a by-product rather than as a waste material. In 1976, over 90% of the slag produced in Canada was air-cooled (6).

Foamed Slag

Foamed slag (sometimes referred to as expanded slag), which is used as a lightweight aggregate, is produced by introducing a limited amount of water to the molten slag. The water vaporizes and the escaping bubbles catch in the solidifying product resulting in a lightweight, porous product. Disadvantages of this process include the high emissions of hydrogen sulphide during foaming and the high absorption of water by the product when used as an aggregate. No expanded slag has been produced in Canada since the 1960's.

Water-Granulated Slag

The most commonly employed method of quenching slag is by water granulation. The molten slag is usually broken up by water jets and is then immediately immersed in water, but several variations are used (4). Although it is an effective method of quenching, water granulation has several disadvantages from environmental and production viewpoints. The quenching water becomes contaminated with sulphur and other compounds leached from the slag, and sulphides combine with the water to form hydrogen sulphide. However, emissions are lower than from air-cooled pits and modern granulators are fully enclosed and are fitted with a stack (Fig. 2.3). Besides potential air- and water-pollution problems the slag can have a high residual-moisture content and must be dried (energy-intensive) prior to grinding for cementitious uses.

The first cements were produced from granulated slag in Europe by Langan in 1863 (1). A history of slag cement production in North America was written by Lewis (7), but as recently as 1978, no granulated blast-furnace slag was being produced in Canada and only a small amount was produced in the United States (6). However, a large-capacity (0.8 million metric tons) granulation and separate grinding plant has been operated by the Atlantic Cement Company at Sparrows Point (Bethlehem Steel), Maryland, since 1982 (8,9) and slag cement is now available along the eastern seaboard of the USA. As well, Lehigh Portland Cement Company has marketed granulated slag in the Chicago area since 1984 from a pilot-scale (0.02 million metric tons) facility at Inland Steel in Gary, Indiana (10). The Waylite Corporation has marketed a granulated slag to the local block industry around Bethlehem, Pennsylvania, for the past four or five years but its operation may be affected by blast-furnace

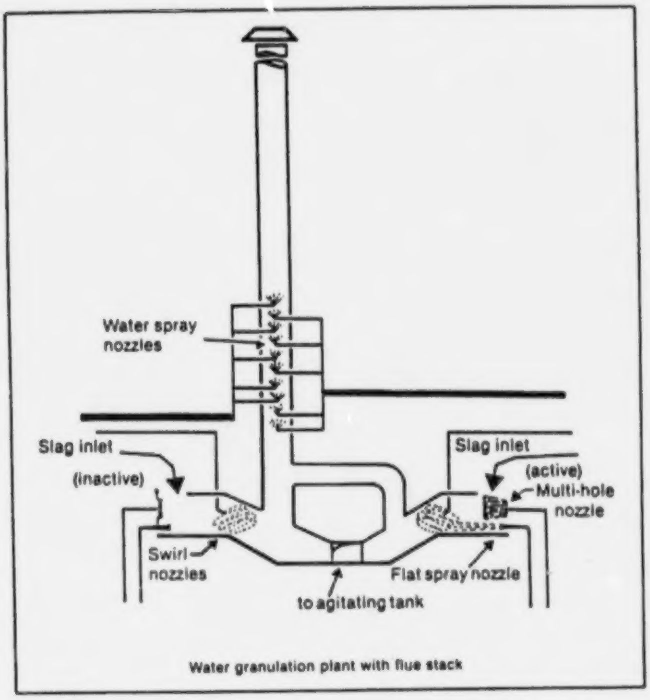
Water spray nozzles
Slag inlet
(inactive)
Slag inlet
(active)
Multi-hole nozzle
Swirl nozzles
Flat spray nozzle
to agitating tank
Water granulation plant with flue stack

Fig. 2.3 — Diagram of a typical modern slag water granulator (9)

closures. In addition, because of the success of Algoma Steel's pilot-scale operation at their plant in Sault Ste. Marie, Ontario (11), a full-scale granulation and grinding plant commenced production in 1986 at Blind River, Ontario. Typical chemical compositions are given in Table 2.1 for slags from Sparrows Point, Maryland; Hamilton, Ontario; and Sault Ste. Marie, Ontario.

The first use of separately ground, granulated-slag cement in Canada was thought to be in 1972 by Castle Cement in Burlington (12). Air-cooled slag was remelted with silica and alumina additions to produce mineral wool. The "waste" from this process was a granulated slag that had higher than normal contents of silica and alumina. To the best of the writer's knowledge, this material was used on a small scale in local ready-mixed concrete for only a few years.

Table 2.1 — Typical chemical compositions of three North American separately ground slags

	Atlantic Cement Company's NEWCEM (Ref. 70)	Standard slag cement Hamilton, Ontario (Ref. 29)	Algoma slag Sault Ste. Marie, Ontario (Ref. 11)
CaO	41.60	40.04	32.34
SiO_2	33.17	37.08	38.35
Al_2O_3	10.80	8.76	8.76
MgO	12.50	11.52	18.64
Fe_2O_3	0.63	1.93	0.61
S*	0.54	1.99	0.95
Na_2O	0.35	0.36	0.22
K_2O	0.50	0.44	0.71
MnO	—	0.72	1.41
TiO_2	—	0.28	0.36
Form	Granulated	Pelletized	Granulated

*Sulphur is almost totally present as sulphide.

Pelletized Slag

The slag pelletizer was developed by National Slag Limited in Canada (13) as a means of bringing under control the high levels of gas emission typical of the "pit-foaming" process. Pelletized slag is produced (Fig. 2.4), by expanding molten blast-furnace slag under water sprays, and then by passing the flow of this pyroplastic material over a spinning drum. On the drum are mounted fins, which break up the slag and fling it in the air for a sufficient time (and distance of about 15 m) that surface tension forms pellets (14). Sulphide gases are trapped inside the pores as the pellets solidify. This concept of using limited water sprays and a finned, rotating drum to quench slag (for cement purposes) had also been used prior to 1909 in England and Germany (15), and since around 1950 in the USSR (16).

In addition to positive control of gas emission, several other benefits of pelletizing slag have been demonstrated. From the point of view of slag handling, the pelletizer takes the molten material, which would normally require several days of air cooling, and turns it into an easily handled product that can be immediately removed from the blast-furnace area. This quick-cooling aspect of pelletizing is important in situations where only limited space is available for slag handling adjacent to the furnace.

Production of a satisfactory lightweight aggregate with low absorption and good thermal-conductivity properties generally results in a fairly crystalline [illegible] structure (17,18). However, by increasing the intensity of the water spray

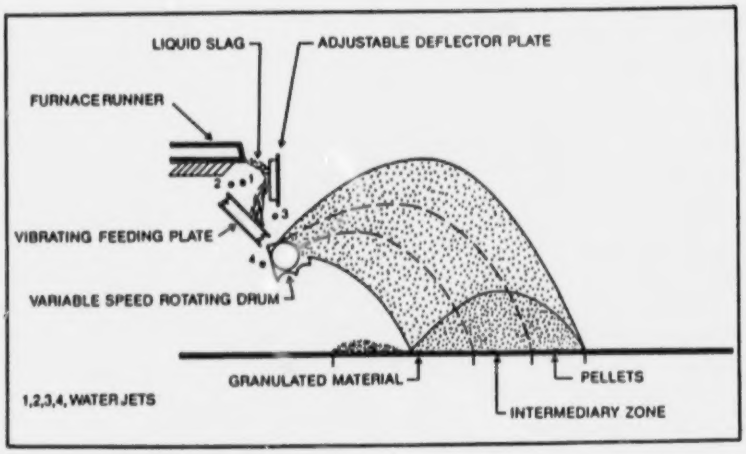

Fig. 2.4 — Diagram of a typical slag pelletizer (9)

and the speed of the spinning drum, it was found that a high degree of vitrification could be obtained, making pelletized slag suitable for cementitious applications. The major advantages of using pelletized slag instead of many water-granulated slag systems for cement production is the low residual-moisture content of the pellets (average 5.5% (17)) resulting in less energy required for drying. Although in recent years, moisture contents had increased to achieve higher glass contents, National Slag Limited has recently improved the pelletizing process and has reduced moisture contents below 6%. Their "Vitrex" pellets now can be ground without pre-drying (19). Because of its more porous structure, pelletized slag may require less energy than granulated slag when grinding to typical cement finenesses.

Also, Kramer (3) reported that the production of a low-density, porous glass, instead of a dense, compact glass, resulted in higher strengths of cements, especially at early ages and with low additions of portland cement. Pelletized slag, as previously mentioned, has the advantage of such a porous structure. Another feature of pelletized slag found by Roper (20) was a much higher variation in chemical composition between slag grains than in granulated slags as detected using an electron microprobe. He postulated that this variability might result from a state of incipient crystallization of the glass. This condition may be advantageous because Hawthorn et al. (21) have suggested that areas of incipient crystallization may act as nucleation sites for hydration.

In Canada, pelletized slag is produced in Hamilton at both the Stelco and Dofasco steel mills with production of about 0.4 million metric tons (22). Whereas about 0.1 million metric tons are currently used as lightweight aggregate in concrete floor slabs and block products, most is used to produce separately ground slag cement (23). Although pelletized slag is still a relatively new product, its use is expanding, with production in eight countries in at least 27 installations in 1976 (19).

In the large, ready-mixed concrete market in southern Ontario adjacent to the steel mills in Hamilton, separately ground pelletized slag has been available since 1976 and is currently used by the majority of concrete producers. It has even displaced fly ash in several instances. In addition to Standard Slag Cement's grinding plant, which has operated since 1976, pelletized slag is being ground separately at St. Lawrence Cement (producing 0.05–0.10 million metric tons) and St. Marys Cement (producing only for its subsidiary companies) in Ontario and Michigan. A granulation and grinding plant (0.2-million-metric-ton capacity) built by Reiss Lime Company Limited near Algoma Steel's Sault Ste. Marie mill commenced production in 1986. Because of its remoteness from large, ready-mixed concrete markets, much of the new Algoma granulated slag will likely be used locally in cemented mine backfill. However, existing port facilities on Lake Huron may be used in future to ship to cities on the Great Lakes.

3. FACTORS AFFECTING SLAG HYDRAULICITY

Major reviews on the hydraulicity of slag were given by Keil (24), Kramer (3), Schröder (1), Satarin (25), and Smolczyk (26). The properties of slag that have been generally accepted as influencing its reactivity are:

- — the degree of vitrification (glass content)
- — the chemical composition
- — the mineralogical composition
- — the fineness of grinding
- — the activation of slag glasses.

Here the published work is summarized in terms of each of these five properties.

Degree of Vitrification

The latent hydraulicity of quenched slag is generally considered to result from the perched Arrhenius energy level of its amorphous structure in comparison to a crystalline structure of the same composition (5). Unlike commercial glasses, the high basicity of slag glass makes its structure only metastable, and it can be completely devitrified by heating to less than 1000°C. At ambient temperatures, crystallization is only inhibited by the high viscosity of the solid.

With slag, the presence of glass is the most significant variable, and certainly the most essential to hydraulic performance, because a non-quenched, crystalline slag possesses little reactive potential. The amount of amorphous material obtained can be controlled by the producer, yet because of its nature (i.e., lack of range order, thus not exhibiting X-ray diffraction (XRD) peaks), the degree of vitrification is the most difficult property of slag to quantify. Thus, although many methods of glass content measurement are available, widely differing results are obtained from each.

Major contributions and summaries on glass structure and determining glass content are available in the literature (1,3,4,24,27,28,29).

One explanation for the hydraulic activity of glasses has been based on considerations of free energy. Although not working with slags, Nassau et al. (30) found that certain glasses hydrated in moist air whereas crystals of the same composition did not. Their explanation of this phenomenon was based on the Gibbs free-energy equation and assumed equilibrium conditions and no kinetic barriers. For the transformations:

glass→crystal $G_{g,c}$ is negative
crystal + H_2O → hydrate $G_{c,h}$ is positive,

where:

G = Gibbs free energy
g = glass
c = crystal
h = hydrate*.

Therefore for the direct hydration of glass:

glass + H_2O → hydrate $G_{g,h} = G_{g,c} + G_{c,h}$.

As long as the magnitude of $G_{g,c}$ is larger than $G_{c,h}$, then $G_{g,h}$ is negative and the glass will hydrate even if the crystal would not. These reactions are illustrated in Figure 3.1. Slags hydrate only very slowly with water. The kinetic barriers to hydration, represented by $E_{g,h}$, can be overcome by alkaline, sulphate, or temperature activation.

The degree of vitrification achieved during quenching depends on several factors; furnace tapping temperature, slag chemistry, slag viscosity, and rate of cooling achieved by the quenching method. The first three factors are interdependent, and determine whether the applied cooling rate is sufficient to prevent extensive crystal formation. The temperature, chemistry, and viscosity of a slag are optimized for blast-furnace operations, the primary function being to produce iron with consistent properties. As a result of modern furnace practice coupled with uniform sources of iron and limestone flux, slags now are consistent in chemistry (i.e., slag viscosity depends mainly on temperature for

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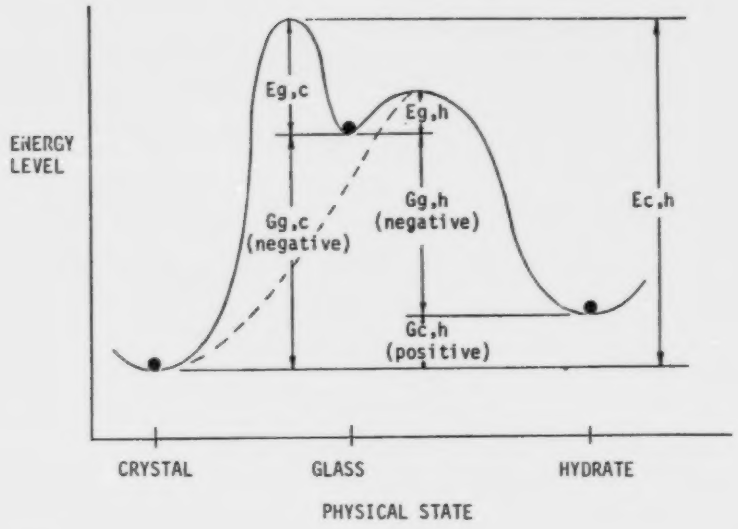
*For convenience, the simplified notation of Nassau et al. is adopted.



LEGEND:

E = activation energy required to overcome the energy barrier to reaction
G = Gibbs free energy
g = glass, c = crystal, h = hydrate

COMMENTS:

Eg,h can be obtained by chemical means, such as alkaline activation, or by high temperature and pressure curing.
Eg,c is obtained by heating to the devitrification temperature around 850°C.
Ec,h can only be overcome directly by very long periods of hydrothermal curing (35 days at 180°C, Speakman, 1970), or indirectly by first remelting and quenching to a glass, then hydrating.

Fig. 3.1 — Conceptualization of Arrhenius-type reactions (31), (using the notation ref. 30)

a specific furnace and burden). As long as the tapping temperature is high enough and a standard quenching process (granulation or pelletization) is used, the resulting glass contents should be fairly constant.

Schröder (1) gave details of how changes in blast-furnace processes influence the resulting slags. From experience in collecting individual slag samples from a number of casts (31), the biggest variable influencing the slag is the temperature at which the furnace is tapped. In spite of modern controls, the furnace can experience "upsets" and hot metal temperatures recorded over a three-month period for one furnace varied from 1390°C to 1590°C (Table 3.1), noting that 75% of the hot metal temperatures were between 1490°C and 1550°C for 46 individual samples. Because the liquidus temperature of typical slags varies from 1320°C to 1450°C (1), the reduction of furnace temperature can result in some crystallization before the slag is quenched. The molten slag was also found by this writer (using an optical pyrometer) to lose about 100–150°C between the furnace tap hole and pelletizing drums, passing along an open 15-m slag runner.

Table 3.1 — Range of chemical compositions for slags produced from one blast furnace* over three months in 1976**

	Weight %		
Element	Minimum	Maximum	Typical
CaO	34.17	43.16	39.98
SiO_2	33.33	43.68	37.53
Al_2O_3	7.57	10.50	8.33
MgO	8.27	13.51	10.06
K_2O	0.14	1.68	0.44
S	1.23	2.98	2.02
Fe_{total}	0.31	1.91	0.44
Mn_{total}	0.28	2.04	0.54
Hot metal temperature (°C)	1390	1590	1510

*Dofasco No. 4 furnace, Hamilton, Ontario, Canada.
**From reference 31.

Blondiau (32) found that reduction of granulation temperatures from just 1538°C to 1479°C resulted in strength reductions of the cement of 10–40%. Fierens and Poswick (33) found that the hydration of completely vitrified, synthetic (laboratory-produced) slags was affected by the quenching rate applied. The higher reactivity of more-quickly quenched slags was found to be the result of fewer defects in the glass structure. However, this trend was not as clear when applied to industrial slags (34). Goto et al. (35) found that the effect of quenching rate on reactivity of synthetic slags was influenced by chemical composition.

Schwiete and Dölbor (36) modified quenching conditions for each of 30 slags and found that the predominant factor affecting strength was glass content (Fig. 3.2). Although increasing crystalline contents reduced hydraulicity, it was thought that slags with glass contents as low as 30–40% could still be employed.

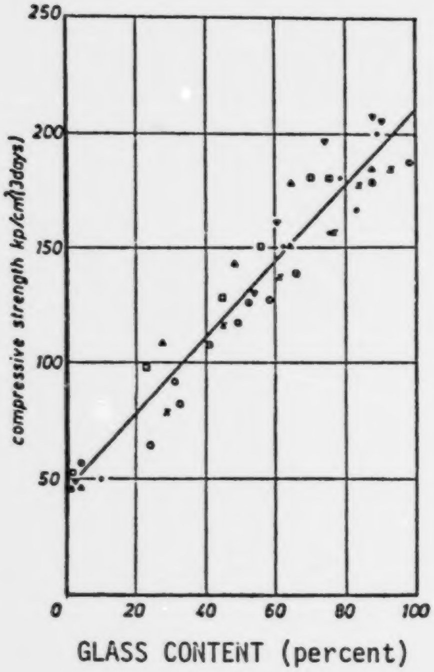


Fig. 3.2 — Relationship between glass content and three-day strength development (after ref. 36), 100 kg/cm² = 9.8 MPa

Other researchers, as Smolczyk (26) pointed out, have not found a linear glass content–strength relationship, and in some cases small amounts of crystalline inclusions were advantageous. As shown in Figure 3.3, Demoulian et al. (37) found that the strengths of slags with glass contents in excess of 95% were reduced. Figure 3.3 also shows that the influence of more than 30% merwinite crystal content on strength development was minimal. They concluded that the composition of the glass fraction was enhanced with regard to reactivity by the merwinite (C_3MS_2) crystallization, and that this counteracted the effect of reduced glass content. This phenomenon has been confirmed by Frearson and Uren (38) who found that the dendritic merwinite crystals were mostly encapsulated in glass and their presence made the particles more reactive. Reduction in strengths with glass contents greater than about 90% were also reported by Frigione (39).

Smolczyk (26) mentioned that, unlike concentrations of large crystals, the presence of finely distributed crystals would have little detrimental effect on strength. The reason for this may be that small, finely distributed crystals could remain partially or totally encapsulated in reactive glass when ground to cement finenesses.

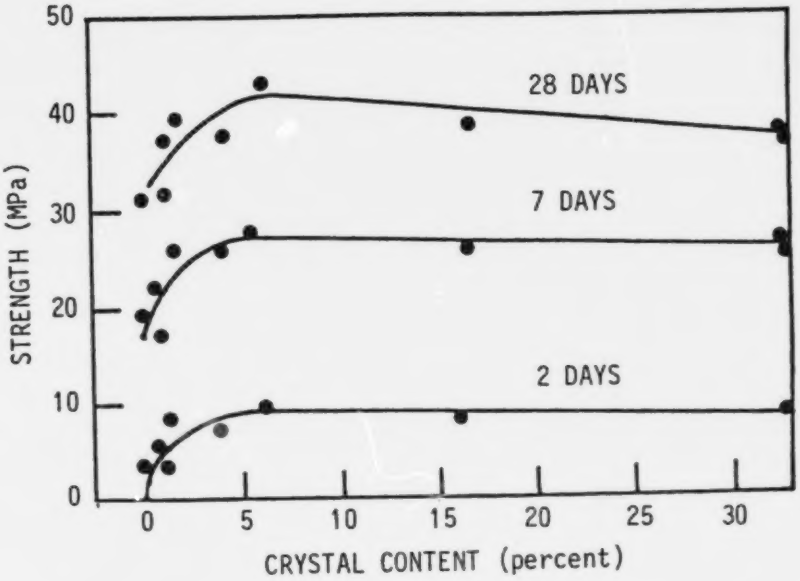


Fig. 3.3 — Relationship between merwinite crystal content and strength development of standard ISO mortars (76% slag, 19% clinker, 5% gypsum) (after ref. 37)

In spite of the fact that a mainly amorphous structure is essential to slag hydraulicity, the inclusion of minimum glass content criteria in standard specifications is rare. One reason for this is that many methods are used to determine glass contents and the results do not always agree. However, even if a standard method were adopted, another problem would be establishing a minimum acceptable glass content. Minimum levels such as 90% have been quoted in commercial data sheets, but as previously discussed, Schwiete and Dölbor (36) suggested that 30–40% glass was acceptable, and the results of Demoulian et al. (37) implied that less than 70% glass was still acceptable. Coale et al. (40), on the other hand, suggested a minimum glass content of 85%, not only to avoid low reactivity but also to reduce the possibility of unsoundness resulting from the crystallization of periclase. However, with the possible exception of some high magnesia (up to 20%) South African slags (41), this latter consideration is not known to be a problem.

Hooton (31), and Hooton and Emery (29) studied several techniques for measurement of glass content and further developed a cross-polarized light microscopy method (referred to as the Modified McMaster Method) which was later adopted as an appendix in the Canadian Standard for Cementitious Hydraulic Slag, CSA A363-M1983. This method was included for checking the degree of vitrification only as no minimum glass-content criteria was included in this or other Canadian standards. CSA and ASTM standards have now adopted more satisfactory direct-strength performance tests with which to judge slag reactivity (CSA CAN3-A23.5-M82, ASTM C989-85). Although the modified McMaster method has been used elsewhere with some success (42), several other techniques have been developed (43,44). The work by Frearson et al. (43), using reflected-light microscopy, is especially important in that it resolved the problem of identifying reactive glassy particles having large, embedded, dendritic merwinite (C_3MS_2) crystals which would previously have been labelled as crystalline. Great Britain appears to be going ahead with a minimum glass-content criteria in spite of trends in other international standards towards performance testing alone (43).

Although a glassy structure is essential to reactivity, a high glass content by any procedure does not guarantee a highly reactive slag. There is no exact correlation of glass content to hydraulicity. A slag producer would probably be unable to reject any underground slag of low glass content, the slag likely being well blended in the stockpile by then. The only feasible method of rejecting incoming material would be by simple observation, because air-cooled slag differs in colour and physical structure from both water-granulated and pelletized slags. Glass content, from the writer's experience, is usually measured on the final product, which if the incoming slag stockpile is properly blended, is consistent in glass content and hydraulic activity.

Chemical Composition

Although the vitreous state is essential to slag hydraulicity, the chemical composition of slag is also an influencing factor. Not only does the composition affect the degree of vitrification achieved upon quenching (for a given quenching process, via effects on liquidus temperature and viscosity) but also it affects the solubility and, hence, the reactivity of the glass during hydration. For example, at ambient temperatures commercial glasses of high silica content are not readily attacked by water or by alkaline solutions, but as the calcium-to-silica (C:S) ratio increases they become more soluble (41). However, as the C:S ratio increases, the slag also becomes more difficult to vitrify for a given quenching process (27).

It is generally accepted that the hydraulic activity of slags increases with increasing contents of CaO and Al_2O_3 and with decreasing contents of SiO_2 and MnO (1,45). However, Smolczyk (26) stated that the so-called acid slags ($C/S<1.0$), which were previously considered of poor quality (3,24), were reactive when the low CaO contents were compensated by increases in MgO and Al_2O_3 contents. This information was of interest because slags produced in Hamilton, Ontario, often have C:S ratios less than unity yet are still very reactive. Furthermore, as Kondo (46) mentioned, slag glasses with increasing Al_2O_3 contents may develop higher strengths, but a factor often overlooked is that these glasses also require higher levels of calcium hydroxide (CH) activation to develop strength. He suggested that this increased CH demand at high Al_2O_3 contents may be the result of pozzolanic rather than of hydraulic reactions and the CH is no longer just an activator. From the literature, the influence of MgO on hydraulicity is conflicting (1,3) but most recent studies have shown it to be beneficial (26). The early concerns about the formation of periclase, which could result in unsoundness, have been diminished by the successful use of South African slags containing up to 20% MgO (41,47,48).

The effect of minor elements on reactivity is unclear. Keil and Gille (49) found that synthetic glasses composed of only the major oxides, C-M-A-S, did not exhibit the same reactivity trends as industrial slags. However, according to Nurse (28), Tanaka et al. found that the reactivity of C-A-S glasses was similar to that of industrial slags. Smolczyk (50) found that the inclusion of minor elements in a complex equation improved predictions of strength but that the effects of these oxides changed with the properties of the portland cement activator and with the different curing ages evaluated.

Although a slag cement producer has no control over the chemical composition of slag (except for the rejection of slags with unusual composition), many of the studies on slag hydraulicity have concentrated on compositional effects (40,51,52,53). From these and other studies, at least 13 compositional moduli have been developed to predict optimum slag compositions, as summarized by Keil (24), Schröder (1), Lea (4), Terrier (54), Gupta (55), Krüger (41), and Hooton (31).

Many of the moduli are derived from the basicity ratios used in blast-furnace operations to judge the melting conditions in the blast furnace, as given in Equations 1–3 (24).

$$M1^{*} = C/S \qquad \text{Eq 1}$$

$$M2 = (C + M) / S \qquad \text{Eq 2}$$

$$M3 = (C + M) / (S + A) \qquad \text{Eq 3}$$

The modulus M3 is also used in the USSR in combination with M4 to evaluate slags for cements (56).

$$M4 = A/S \qquad \text{Eq 4}$$

Before 1942, the German DIN 1164 cement standard required that Equation 5 be at least unity for slags used in cements.

$$M5 = (C + M + 0.33A) / (S + 0.67A) \geq 1.0 \qquad \text{Eq 5}$$

But this was replaced by Equation 6 which was still contained in the 1967 revision of DIN 1164.

$$M6 = (C + M + A) / S \geq 1.0 \qquad \text{Eq 6}$$

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*The compositional ratios or moduli listed here are labelled M1–M13 for convenience.

In Japan, the modulus M6 is required to be greater than 1.4 (25,57).

Another modulus, M7, was given by Keil (24) which included terms for calcium sulphide (CaS) and manganese contents in slags.

$$M7 = (C + CaS + 0.5M + A) / (S + MnO) \geq 1.5 \qquad \text{Eq 7}$$

Equations 5, 6, and 7 are mentioned in a note in CSA Standard A363-M1983 as guidelines for desirable slag compositions, but there are no compositional requirements in this Standard.

De Langavant (51) proposed an index of quality,

$$M8 = 20 + C + A + 0.5M - 2S \qquad \text{Eq 8}$$

in which the slag quality was judged medium if $M8 < 12$, good if $12 < M8 < 16$, and very good if $M8 < 16$. However, if this index is applied to typical, modern, North American slags in which dolomite is used as the blast-furnace flux (see Table 2.1), almost all would only be of medium quality.

Sopora (52) considered iron and manganese to have adverse effects on reactivity and proposed the ratio given in Equation 9.

$$M9 = (C + M + A) / (S + F + (MnO)^2) \qquad \text{Eq 9}$$

Schwiete and Dölbor (36) did not consider the effects of magnesia in the development of their modulus, which was rearranged by Krüger (41), as shown in Equation 10.

$$M10 = (C + 0.9A) / (S + 0.1A) \qquad \text{Eq 10}$$

Cheron and Lardinois (58) found a linear relation between Equation 11 and compressive strength.

$$M11 = (C + 1.4M + 0.56A) / S \qquad \text{Eq 11}$$

Coale et al. (40), using synthetically prepared glasses over a wide range of major oxides, found a relation between compressive strength and Equation 12 for calcium hydroxide activation.

$$M12 = (6C + 3A) / (7S + 4M) \qquad \text{Eq 12}$$

But at the same time, it was found that neither this modulus nor the previously mentioned moduli were entirely satisfactory even when applied to an individual phase field. It was concluded that no linear relationship exists between strength and oxide composition over a large range of compositions. Gupta (55), Regourd et al. (59), and Hooton and Emery (29) also found that the prediction of strength development either by chemical composition or by many of the previously given moduli was unsatisfactory.

Parker and Nurse (27) recognized that the glass content was important to any quality calculation and incorporated it (determined microscopically) into their formula along with the product of glass content and the ratio, M5;

$$M13 = 0.38\ (\text{glass content})\ (M5 - 0.72) + 75.0 \qquad \text{Eq 13}$$

where M13 is the percentage compressive strength developed in comparison to concrete made from portland cement. Kramer (3) also found a relationship between strength and glass content as measured by ultraviolet light multiplied by the ratio M1. In these two relationships, the assumption of perfect vitrification (which is made in ratios M1–M12) is not made and these indices, combining glass contents and chemical compositions, appear to be more applicable to the evaluation of industrially quenched slags. However, Parker (60) subsequently reported that in spite of their index, M13, strength testing was still the most satisfactory method of evaluating slag quality.

In conclusion, although chemical composition undoubtedly affects slag reactivity, the effects of compositional changes on hydraulicity are unclear. Also, as the composition of slag is determined by the iron producer to optimize the quality of the iron, the work in this area seems disproportionate to its practical use. In practice, blending of unground slag stockpiles is used to ensure relatively uniform properties and hydraulic performance in slag (29).

Mineralogical Composition

Small changes in chemical composition can have large effects on the mineralogical composition of portland cement. The mineralogical composition, rather than the chemical composition, determines its hydraulic properties. Thus, the mineralogical composition of slag glass might be a more significant influence than its chemical composition on its reactivity. The crystalline compounds found in devitrified slag are mainly the melilite solid solution series with end members akermanite (C_2MS_2) and gehlinite (C_2AS) with lesser amounts of monticellite (CMS), diopside (CMS_2), merwinite (C_3MS_2), and others (61,29). However, these crystalline minerals are generally considered inert towards water (1,4), likely because of the regular co-ordination of the atoms in their crystal structures (62). For industrial slags, in which the proportions of the melilite solid solution cannot be deduced by chemical composition alone, Ervin and Osborn (63) developed an X-ray diffraction technique, based on measurements of the average shift in d-spacings.

Keil and Gille (49) concluded that the hydraulic properties of glass could not be evaluated by calculation of the minerals present at equilibrium. Nurse (28) agreed that this technique could be misleading and that it offered no advantages over the more common relations with oxide composition. However, more recently, Regourd et al. (59) concluded that the melilite composition, based on measurement of the lattice parameters of devitrified slags, was an important factor affecting reactivity. Solacolu (64) and Teoreanu and Georgescu (53) found that variations of strength development with chemical composition were not continuous at phase boundaries defining different potential equilibrium mineral formations (some phase boundaries are shown in Fig. 2.2). Therefore, from the conflicting results reported in the literature, the relevance of equilibrium mineralogical composition to hydraulic activity is unclear.

Akatsu et al. (65) found that in the gehlinite–akermanite system, the most reactive glasses for three- and seven-day strengths, had a composition of

30–50% akermanite. However, at 28 days high strengths were obtained from a wider range of glasses with compositions of 20–70% akermanite.

Kondo and Ueda (66), based on a study of the pH of glasses suspended in water, considered C_2MS_2 more than just latently hydraulic, whereas C_2AS and a solid solution mixture were considered just latently hydraulic. Crystalline inclusions contained in quenched slags, such as C_3MS_2, which are not present after equilibrium crystallization (41), may affect slag reactivity by altering the composition of the glass phase. Schröder (1) mentioned work done to enhance hydraulicity by thermal treatments to promote favourable, unstable crystallizations of merwinite with respect to gehlinite. Again, this effect has been confirmed in Frearson et al. (43). Similarly, although merwinite crystals were found in samples of incompletely vitrified (84–96% glass) pelletized slag from Hamilton, Ontario (29), when the same slags were devitrified (by reheating to 1050°C and slow-cooling), merwinite was not present as an equilibrium phase.

Fineness of Grinding

Although the ease with which slag can be ground does not affect its hydraulicity, it does affect the optimum fineness of grinding from both strength development and economic viewpoints. Water-granulated slag has been reported to be less easily ground than portland cement (67), thus intergrinding, the traditional method of producing blended cements, would tend to grind the portland cement component preferentially. However, work by Osborne (68) has shown that pelletized slag, because of its porous structure, requires less energy to grind than do granulated slags. As summarized by Daimon (57), increasing the fineness of the slag component results in better strength development of the blend and, with intergrinding, this is difficult to achieve.

Because of its advantages, as summarized by Schröder (1), Stutterheim (67), Lea (4), and Mills (5), the practice of separately ground slag has developed in South Africa, England, Canada, and, more recently, in the United States. Whereas a Blaine fineness of 400 m^2/kg has been adopted for some Canadian pelletized slags in commercial operations (17,69), Atlantic Cement's separately ground slag in the USA is typically in the range of 500–550 m^2/kg (70) and Reiss Lime's new plant near Sault Ste. Marie is producing at a fineness of 450 m^2/kg. As well, both the Atlantic Cement and Reiss Lime plants have efficient closed-grinding circuits that can control particle size.

Lea (4) reported the influence of fineness on the 28-day strengths of concrete containing 30% slag cement. Strengths were decreased by 22% when the Blaine fineness of the slag was reduced from 393 m^2/kg to 310 m^2/kg, but only increased by 13% when the slag fineness was increased from 393 m^2/kg to 485 m^2/kg. However, at 75% slag contents, Schröder (1) reported almost equivalent increases in strengths for slag finenesses increased from 350 m^2/kg to 400 m^2/kg and 400 m^2/kg to 450 m^2/kg (Fig. 3.4). For the same slag content, Schröder (1) also found that the effects of fineness on strength were also influenced by the chemical composition of the slag. Depending on the composition, the increases in 28-day strengths varied from 20–60% when the fineness was increased from about 280 m^2/kg to 400 m^2/kg.

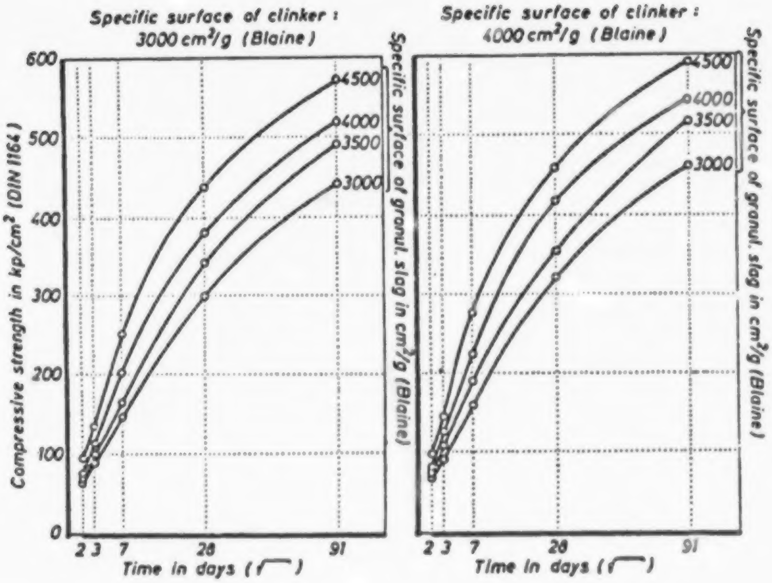

Fig. 3.4 — Effect of fineness on strengths of DIN 1164 mortar prisms containing 75% slag (1)

With a Canadian pelletized slag ground to Blaine finenesses of 328, 363, 403, and 454 m^2/kg, Hooton and Emery (29) found that mortar cube strengths (70% slag) at seven days were almost unaffected. At 28 and 91 days, strengths increased with fineness except that the 403 m^2/kg and 454 m^2/kg slag strengths were similar.

In general, as with all cementing materials, the reactivity of slag is proportional to its surface area, with the fineness being limited by economic considerations as well as by performance considerations such as shrinkage and setting times.

Activation of Slag Glasses

The reaction mechanism by which the latent hydraulicity of slag glasses is released was proposed by D'Ans and Eick (71). In water, CaO was initially released from the surface of the slag grains, but the reaction of water with the remaining Al_2O_3 and SiO_2 formed impermeable acidic gels on the surfaces of the slag grains. These coatings acted to inhibit further hydration until sufficient, externally supplied lime was added to dissolve them. This mechanism was confirmed by Kondo and Ueda (66) for C_2AS glasses where 0.2-μm thick coatings of composition ASH_6 were found to form on the glass surfaces.

According to Eitel (74) and D'Ans and Eick (71), found that slags high in calcium sulphide were self-activating because, in water, CaS dissolved to form $Ca(OH)_2$ and H_2S. Because of the desulphurization processes used at Dofasco in Hamilton, Ontario, slags with sulphide contents as high as 3% were found (see Table 3.1) and this may account for some of the non-activated reactivity found for these slags (14,55,75). In fact, the Canadian Standard for Cementitious Hydraulic Slag, CSA A363-M1983, includes a strength-development test for pure slag mortars. However, Teoreanu and Georgescu (53) and Krüger (41) found that there was no relationship between the strength potential of unactivated and activated slags and, therefore, there appears to be little value in evaluating the hydraulic potential of an unactivated slag.

The most commonly used activators have been calcium hydroxide, portland cement, and gypsum. Other chemical activators, such as Na_2CO_3 (76), NaOH, and Na_2SiO_3 (45,77), have also been used. From the practical point of view, portland cement is the most important activator because it is present in almost all concrete.

It is often assumed that when portland cement is used, the activation is actually by the calcium hydroxide liberated as the portland cement hydrates. However, Nurse (28) mentioned that there are differences between lime and portland cement activation and the type and amount of activation required for optimum strength depend on the slag composition. Keil and Gille (49) found that when using lime, C_2AS glass developed high strengths whereas C_2MS_2 did not, but the reverse was true when portland cement was used. In contrast, Krüger (41) suggested that the hydration reactions of slag activated with hydrated lime and portland cement are similar, and that lime should be used instead of portland cement for evaluation of slag's strength potential.

The activation of slag by portland cement also depends largely on the mineralogical composition of the portland cement (26). Larger amounts of C_3S have been found to be beneficial (78). However, Frigione and Sersale (79) did not find a relationship with C_3S. Instead, they found that the most significant factor affecting strength development with 30%, 50%, and 70% slag blends, was the total alkali content of the portland cement clinker. Although higher alkali levels retarded clinker hydration, they accelerated the hydration of the slag component. The hydration temperature is also a factor when evaluating hydraulic potential. Maiko et al. (78) using 50% portland cement–50% slag glass blends found that the composition of glasses developing high strengths at 20°C (CAS_2, CMS, and melilite solid solutions) were not necessarily the same as those at 90°C (αCS, CAS_2, and C_2MS_2).

Ludwig (73) found that the hydration products of portland–slag cements were the same as for portland cement, except that, at higher slag contents, smaller quantities of calcium hydroxide and $C_4(A,F)H_{13}$ hydrogarnets were found.

Smolczyk and Romberg (80) mentioned that the inclusion of slag affected both the porosity and the pore-size distribution of pastes at ambient temperatures. Increasing the slag content of pastes from 0% to 76% had the effect of reducing the volume of large pores (greater than 300-μm diameter) by about one-third. This effect is important because the presence of large capillary pores both increases the permeability and decreases the strength of cement pastes (81). Since then, similar results have been found by Manmohan and Mehta (82), Feldman (83), Roy and Idorn (84), and Hooton (85). Hooton (85) also found reduced permeabilities to water at 91 and 182 days.

4. SLAG REACTIVITY IN AUTOCLAVE-CURING

Autoclave-curing is discussed initially to provide a background, then the use of slag in autoclave-curing is introduced.

Autoclave-Curing Cycles

Autoclave-curing refers to curing at temperatures in excess of 100°C in saturated steam. The terms hydrothermal-curing and high-temperature-and-pressure curing can also refer to autoclave-curing but may also include curing at other than saturated-steam pressures.

Autoclaving is most often employed to cure concrete brick and block and calcium silicate brick (sand–lime brick). In a typical commercial process the binder and aggregate components are mixed in the same manner as normal concrete but with much-lower water contents. Specific amounts of the zero slump mixes are vibrated in moulds until a constant specimen height is achieved. The formed blocks or bricks are then immediately de-moulded and are loaded onto racks. The racks, mounted on wheeled carts, are usually placed in "kilns" and are moist-cured at 60–70°C for several hours to develop the "green" strength needed to resist damage from both handling and thermal stresses. The carts are then loaded into long, cylindrical, pressure vessels where steam is admitted until the maximum temperature (and dependent steam pressure) are reached in one to two hours. Commonly used maximum temperatures range from 160°C to 190°C (0.55–1.17 MPa steam pressure) (86) and these are maintained for two to eight hours, depending on the working schedule of the plant. At the end of the curing cycle the steam is usually released (and used to heat a second pressure vessel) with atmospheric pressure obtained in 0.3–0.5 h. The carts are unloaded, and upon cooling the blocks are ready for use.

Use and Advantages of Autoclaving

Autoclaving was first used in the United States in 1868 (87) but did not develop until Menzel's (88) extensive research on autoclaving and on the use of silica to replace part of the portland cement.

Because of the capital costs involved with building such a plant, and, more recently, the energy costs of producing steam, autoclave-curing is not used extensively to produce concrete blocks in North America. However, until the 1980's, southern Ontario was an exception with about 90% of the blocks being autoclaved (86). However, as a result of high energy costs, this percentage has decreased dramatically.

Besides producing products that have strengths equivalent to 28-day moist-cured concrete in only a few hours, other advantages to autoclaving were summarized by Nurse (89) and the American Concrete Institute (87).

These included:

- reduction in the portland cement or lime required, by partial replacement with ground quartz (which only becomes reactive at temperatures greater than 100°C as shown in Fig. 4.1);

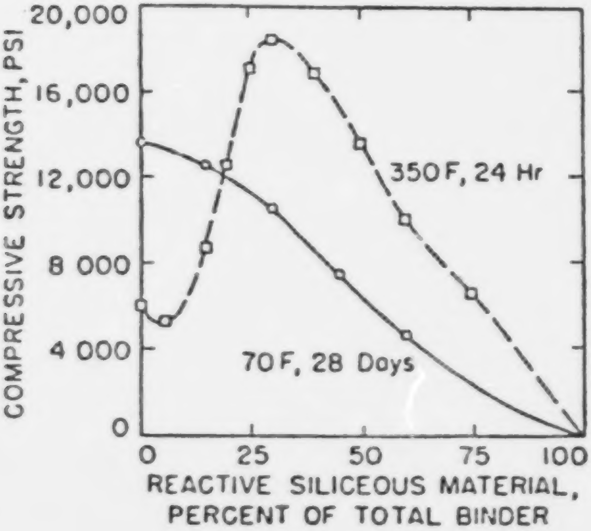

Fig. 4.1 — Compressive strength of autoclaved and moist-cured cement paste with various amounts of silica flour (ground quartz) (after ref. 87)
Note: 1 MPa = 145 psi; 70°F = 21°C; 350°F = 177°C

- increased strength by reaction of the aggregates with the binder (and stabilization of some unsound aggregates);
- reduction in drying shrinkage by about 50%;
- increased resistance to sulphate attack;
- elimination of efflorescence.

The final products also have a low residual moisture content, which, coupled with reduced drying shrinkage, allows their immediate use.

Autoclave Reactions

The nature of autoclave hydration products is similar to those found in concrete cured at ambient temperatures with the following exceptions:

1. The calcium-to-silica (C:S) ratios of autoclave hydrates that result in maximum strengths are much lower, ranging from 0.81 to 1.5.
2. Silica flour (ground quartz), which is almost inert at ambient temperatures, reacts with the calcium hydroxide liberated by the hydration of portland cement at temperatures greater than 100°C to form more calcium silicate hydrates. This reduction or elimination of calcium hydroxide is the major reason for increased sulphate resistance. Silica flour is usually blended with portland cement to provide a C:S ratio consistent with high strengths.
3. The degree of crystallinity of the C-S-H* found in autoclaved hydration products is much higher than the nearly amorphous C-S-H formed at ambient temperatures.
4. Autoclaved portland cement was found (90) to have a low surface area resulting from a collapsed structure with high volume stability.

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*C-S-H is the term used to represent poorly crystalline, variable composition, calcium silicate hydrates of the tobermorite group.

5. STUDIES OF AUTOCLAVED SLAG

Although the use of slag in pastes, mortars, and concrete has been the subject of many studies, little work has been directed to its use in autoclave applications, so a fairly complete summary of these studies is presented here. Many of these studies have used slags or synthetic glasses containing mainly CaO, Al_2O_3, and SiO_2, without dealing with the MgO contained in slags typical of North American production. Also many of the studies on autoclaving slag (and portland cement (91)) concentrate on equilibrium products of hydration at higher temperatures and longer autoclaving periods than those used commercially. Therefore, the results obtained in many of the studies should be viewed with caution when trying to apply them to commercial products.

Synthetic Glasses and Slags without Activation

Negro (92) mentioned that he had studied the autoclave reactions of melilite glasses with various proportions of vitreous C_2AS and C_2MS_2. Hydration products detected were αC_2SH and C-S-H with xonotlite and plazolite at higher temperatures. Because no $Mg(OH)_2$ was detected, it was assumed that the magnesium ions substituted for calcium ions in the calcium silicate hydrates detected. This result agreed with those of Schwiete et al. (93) who found that increasing MgO contents in the melilite glasses resulted in expansion of the lattice of C_2ASH_8 for hydration at 22°C.

However, Krüger and Visser (94), Visser et al. (95), and Krüger (41) found no evidence to support the formation of a C-M-S-H phase in pastes autoclaved at 215°C for up to seven days. In these studies, it was found that a glass of composition C_2MS_2 hydrated to serpentine ($M_6S_4H_4$) and to an unidentified phase (either C-S-H or calcite) with an X-ray diffraction (XRD) peak at 3.027 Å. Amorphous gehlinite (C_2AS) hydrated to the hydrogarnet plazolite ($C_3AS_2H_2$), boehmite (γAH), and possibly αC_2SH. A glass with proportions of 50% C_2AS and 50% C_2MS_2 and a South African slag (MgO = 15.1%) both hydrated to form plazolite ($C_3AS_2H_2$), aluminum serpentine ($M_5AS_3H_4$), and possibly αC_2SH. Therefore, it was concluded that the magnesium in slag glasses did not combine in a C-M-S-H phase but only in MSH phases. Krüger (41) stated that the possibility existed that water selectively attacked certain cations, leaching them out of the vitreous slag to form hydrated phases. The cations not accounted for in the hydration products might then remain in the unhydrated glass network.

Mascolo et al. (96) autoclaved synthetic glasses at 175°C and found the serpentine $M_5AS_3H_4$ together with C_2AH_6 and plazolite. The amount of C_2AH_6 increased with increasing MgO contents whereas the plazolite content diminished. For glasses with a constant (C+M):S ratio, strengths generally increased with increasing MgO content, up to 17.4%.

Govorov (97) autoclaved synthetic C-M-A-S glasses containing 5% MgO at 150°C, 200°C, and 250°C for up to 48 h. For 150°C and 200°C autoclaving the main phase found was CSH(B) (C-S-H with $C/S \geq 1.5$), with hydrogarnets of the solid solution series $C_3AS_zH6_{6-2z}$ (where $z = 0\text{-}3$) forming at some compositions. The highest strengths were found to correspond to maximum hydrogarnet compositions, however, those glass compositions were much different than those typical of blast-furnace slags.

Slags Activated with Gypsum

Massidda and Sanna (98) autoclaved compacts of Italian slag (MgO = 5.5%) activated with 5% gypsum at 180°C for 15 h and 72 h. The only hydrated phase detected was plazolite, with larger quantities present at 72 h but with little difference in strengths. They attributed the high strengths obtained at 130°C (compared to 50°C, 70°C, 120°C, and 150°C) to the lower porosities and finer pore-size distribution found.

Slags Activated with Lime and Quartz

Midgley and Chopra (99) autoclaved ground, foamed, and granulated slags with various proportions of hydrated lime at 160°C for various periods. Unlike fly ash, quartz, and other siliceous materials which consumed large quantities of lime, the slags only fully reacted with 10% lime after at least 6 h at 160°C. The optimum amount of lime activator was found to be 5%, resulting in high strengths (Fig. 5.1). Hydrated phases included a hydrogarnet (C_3ASH_2), tobermorite-like C-S-H, and αC_2SH. When higher contents of lime were added, strengths decreased as the amount of αC_2SH increased at the expense of the C-S-H. The poor strength qualities of αC_2SH were also found by Kalousek (100) for portland cement–quartz pastes. The slags, without lime, hydrated to poorly crystalline C-S-H and a hydrogarnet after autoclaving for 16 h.

Kondo et al. (101) studied the reaction of pastes containing 80% slag (MgO = 3.4%) with 20% lime autoclaved for various periods at 181°C and 213°C. After autoclaving for 0.5 h, 2 h, and 6 h at 181°C, only poorly crystalline C-S-H (composition $C_{1.45}S_{0.8}H_{1.6}$ at 6 h) was detected and further autoclaving resulted in reduced strengths which were thought to be the result of increased quantities of hydrogarnet. This result disagrees with the higher strengths of pastes containing hydrogarnet found by Govorov (97). It was also found that there was high reactivity up to 0.5 h autoclaving, then an almost dormant period occurred until 2 h with the reaction rate increasing at later ages.

The dormant period was attributed to an impervious coating similar to the coatings described by D'Ans and Eick (71) forming on the slag grains and temporarily inhibiting further reaction. A slag–lime paste of the same composition was also autoclaved by Abo-El-Enein et al. (102) with similar hydration products forming, but with slightly different strength development.

In the same study, Kondo et al. (101) autoclaved a paste composed of 50% slag, 20% lime, and 30% ground quartz. For the first 2 h of autoclaving a high-lime, poorly crystalline C-S-H was formed and little quartz was reacted. For up to 12 h autoclaving, increased quantities of C-S-H with lower C:S ratios were

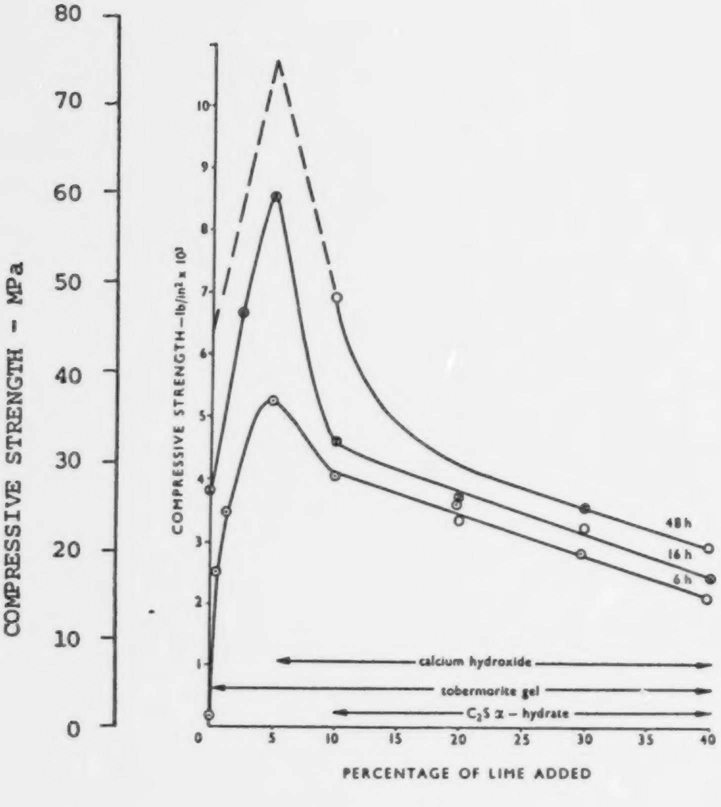

Fig. 5.1 — Relationship between compressive strength and percentage of lime added to granulated slag for various periods of autoclaving at 160°C (99)

detected as strengths increased (composition = $C_{1.5}Ao{\cdot}_1So{\cdot}_9H_{1.05}$ at 6 h). Lower strengths occurring after longer autoclave periods were attributed to a change in morphology of the C-S-H. It was concluded that the high reactivity of the slag after short periods of autoclaving initially inhibited the reaction of the quartz.

Abo-El-Enein et al. (102,103) studied a paste of 25% slag, 25% lime, and 50% quartz autoclaved at 181°C. After 2 h autoclaving, only poorly crystalline C-S-H was detected with more crystalline fibrous C-S-H forming after 6 h, corresponding to optimum strength. Strengths deteriorated after 12 h autoclaving but started to improve after 24 h and a dense C-S-H with a mix of fibrous and platy morphologies was observed in the scanning electron microscope (SEM).

Slag Activated with Portland Cement and Quartz

The study of slag in conjunction with portland cement and quartz was thought to be the most relevant to commercial practice because of the frequent use of portland cement and quartz in autoclave binders.

Menzel (88) substituted ground, air-cooled slag for quartz in portland cement–quartz mixtures of varying proportions. Because of the crystalline nature of the slag, the strengths decreased almost linearly with increasing slag content after 24 h autoclaving at 177°C. In a similar study by Kalousek (100), replacing quartz with ground, expanded slag resulted in lower strengths. Akaiwa and Sudoh (104) found that replacing 45% of portland cement by granulated slag lowered strengths after 5 h autoclaving at 200°C. Yang (45) autoclaved suspensions of 75% slag and 25% portland cement, with and without silica flour, for 16 h at 183°C. Without silica flour, tobermorite-like C-S-H, a hydrogarnet, and possibly xonotlite were detected. With increasing contents of silica flour, the amount of C-S-H increased and the hydrogarnet decreased until it was not detected with 30% silica flour.

An autoclaved slag–portland cement paste was studied by Kamel (105). It consisted of 80% slag, 15% portland cement clinker, and 5% gypsum and was autoclaved at 193°C for 5 h and 6 h. Another paste consisting of one part of the same mixture with 0.5 parts of quartz was also made. After 5 h autoclaving, the paste with quartz was found to contain mainly tobermorite (C-S-H) whereas the paste without quartz also contained a little hillebrandite (βC_2SH). After 6 h autoclaving, xonotlite (C_6S_6H) was also detected, which was thought to be responsible for the lower strengths encountered (106).

In a later study, Kamel (107) found that increasing the temperature from 193 to 204°C and to 213°C reduced the autoclave time required for maximum strength from 5 h to 4 h and 3 h, respectively.

Autoclaving portland cement–slag glass mortars at 175°C, Mascolo et al. (96) found that optimum strengths occurred for glasses with 10% MgO and that the optimum strengths were not sensitive to the amount of portland cement used (30, 50, or 70%). When only 30% slag was used, the influence of slag composition on strength was minimal.

Hooton and Emery (108) and Hooton (31) found that ternary combinations of pelletized slag, portland cement, and silica flour (ground quartz) resulted in higher compressive strengths of mortar cubes, when autoclaved at saturated steam pressures for 4 h at 185°C, than any binary combination of portland cement and slag or portland cement and silica flour (Fig. 5.2). (Berry (109) made similar observations with mortar cubes of ternary compositions of portland cement, slag, and fly ash hydrated at 23°C.) Optimum strengths of mortar cubes were for mixtures of 60–75% slag, 10–20% silica flour, and only 15–20% portland cement. For paste cylinders made with the same materials, but without the ASTM C 778 quartz mortar sand, optimum strengths moved to combinations with around 40% silica flour (Fig. 5.3). Therefore, it appeared that the quartz mortar sand, although having a low surface area relative to silica

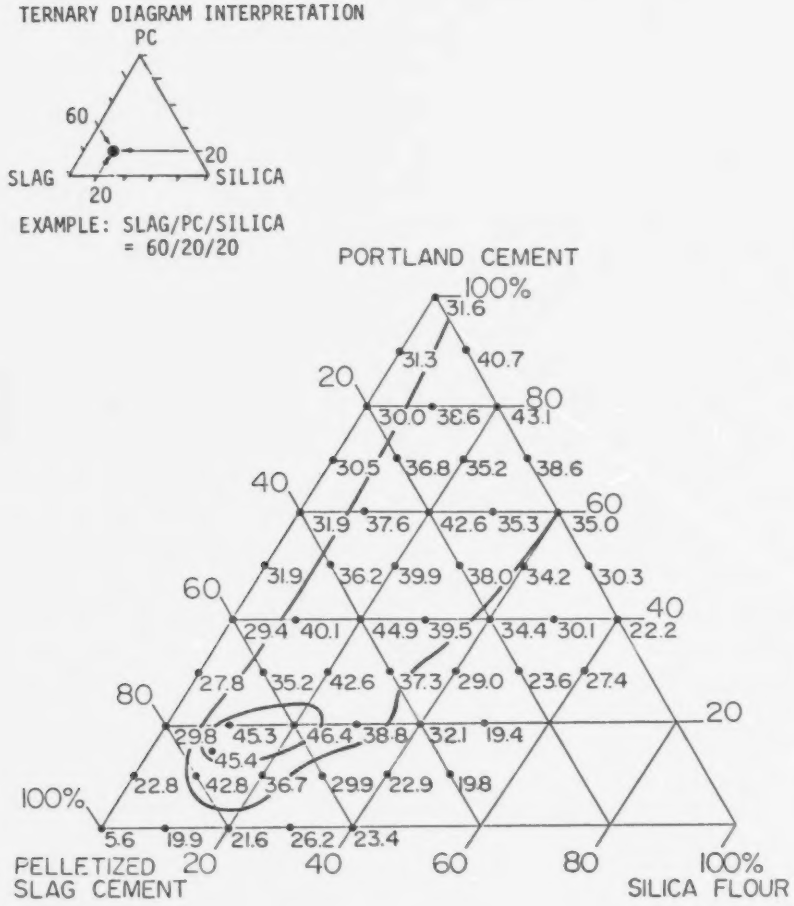

Fig. 5.2 — Compressive strengths of autoclaved mortar cubes (MPa) with ternary slag, portland cement, and silica flour binders. Strength isobars are shown for 35 and 45 MPa (108)

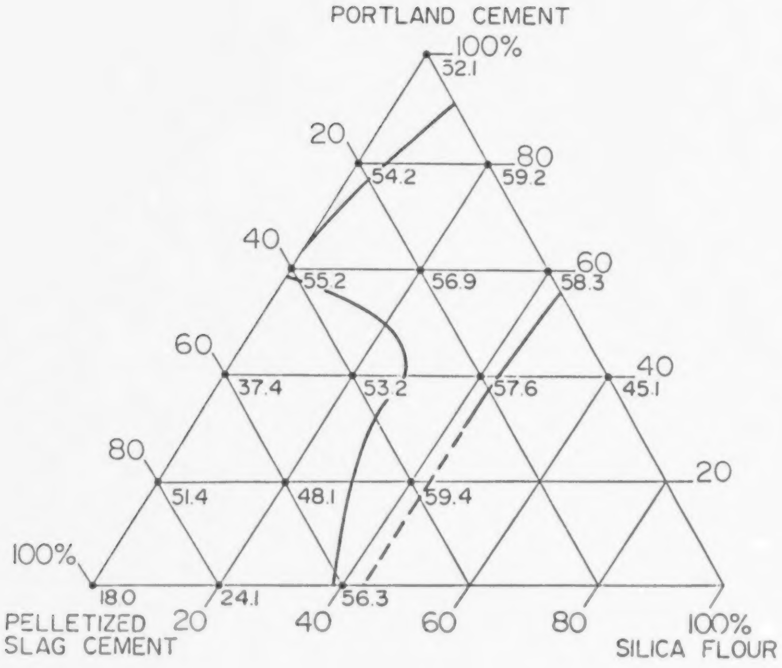

Fig. 5.3 — Compressive strengths of paste cylinders (MPa). The interpolated strength isobar at 55 MPa is shown (108)

flour, entered into the autoclave reactions. By XRD, most of the high-strength paste compositions were found to contain relatively well-crystallized, 11-Å tobermorite and only traces or no αC_2SH (Fig. 5.4). Also, when a sufficient quantity of slag or silica flour was used, the calcium hydroxide content of the autoclaved pastes reduced to below the detection limit of XRD.

In addition, extensive field trials of similar ternary binder compositions in autoclaved block were made at a local concrete-block plant (6,31). However, for economic reasons, instead of using ground slag cement, some of the pelletized slag, semi-lightweight aggregate was partially pre-ground in a high-speed, intensive concrete mixer, prior to insertion in the concrete batch mixer. This partial pre-grinding resulted in production of between 20% and 30% of minus 75-μm material with a Blaine fineness of 285 m^2/kg. When only the minus 75-μm fraction was considered as binder, optimum strength block (autoclaved for 2.5 h at 180°C) was obtained with ternary combinations of 67% slag, 13–20% silica flour, and 13–20% portland cement. The strengths of autoclaved blocks made with both pelletized slag and limestone aggregates are shown in Figures 5.5 and 5.6, respectively.

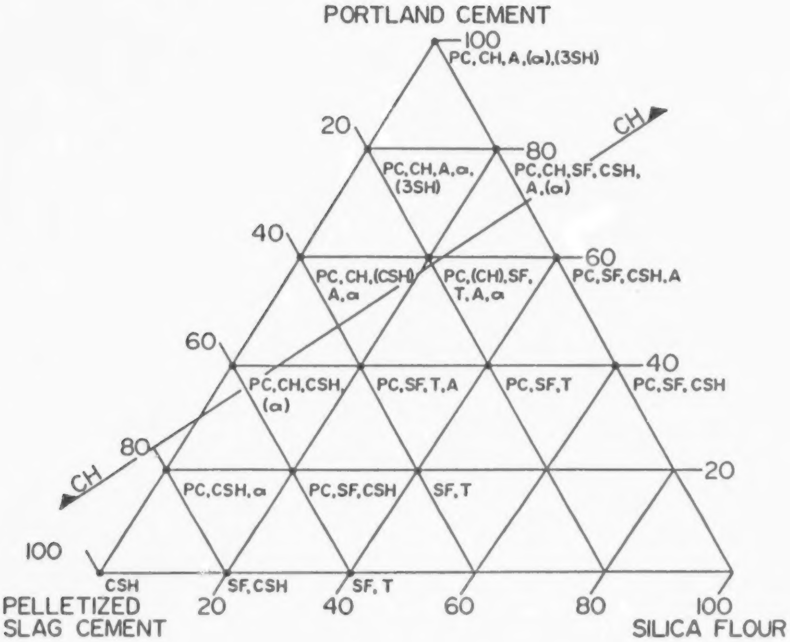
PORTLAND CEMENT
100
PC, CH, A, (α), (3SH)
20
CH
80
PC, CH, A, α, (3SH)
PC, CH, SF, CSH, A, (α)
40
60
PC, CH, (CSH) A, α
PC, (CH), SF, T, A, α
PC, SF, CSH, A
60
40
PC, CH, CSH, (α)
PC, SF, T, A
PC, SF, T
PC, SF, CSH
80
CH
20
PC, CSH, α
PC, SF, CSH
SF, T
100
CSH
SF, CSH
SF, T
PELLETIZED SLAG CEMENT
20
40
60
80
100
SILICA FLOUR

Fig. 5.4 — Phase composition of hydrated pastes (108)

Legend: ***SF = unreacted silica flour***
PC = unreacted portland cement
CH = calcium hydroxide
A = amorphous C-S-H
CSH = semi-crystalline calcium silicate hydrate (C-S-H)
T = more crystalline C-S-H (11-Å tobermorite)
α = αC_2SH
3SH = tricalcium silicate hydrate
( ) = less than 5% detected

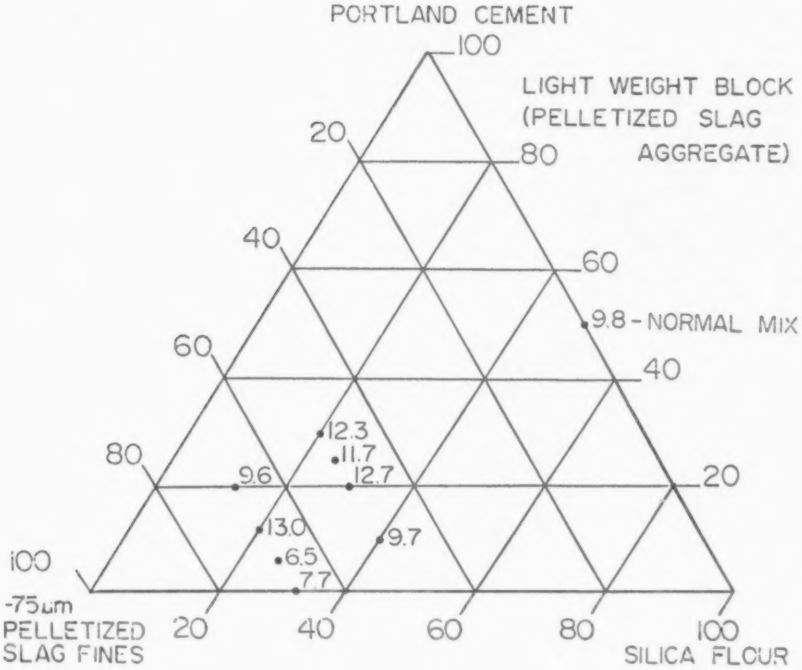

Fig. 5.5 — Compressive strengths of lightweight autoclaved blocks (31)

200 x 200 x 400 mm (MPa, gross area)
CSA minimum = 6.9 MPa
Autoclave cycle 8 h total, 6.2 h at 185°C

Slag Activated with Quartz

Kamel (105) studied a paste composed of 67% slag and 33% quartz with W/C = 0.25. After 5 h autoclaving at 193°C, mostly tobermorite (C-S-H) and a small amount of xonotlite were detected. After 6 h, more xonotlite formed at the expense of tobermorite resulting in a lower value of combined water.

Hooton and Emery (108) and Hooton (31) found that for an autoclave period of 4 h at 185°C, the low strength of pure slag mortars and pastes were generally enhanced by partial replacements with up to 30–40% silica flour (see Figs. 5.2 and 5.3). As well, the ill-crystallized C-S-H binding the pure slag paste was replaced by more crystalline 11-Å tobermorite (see Fig. 5.1). Another interest-

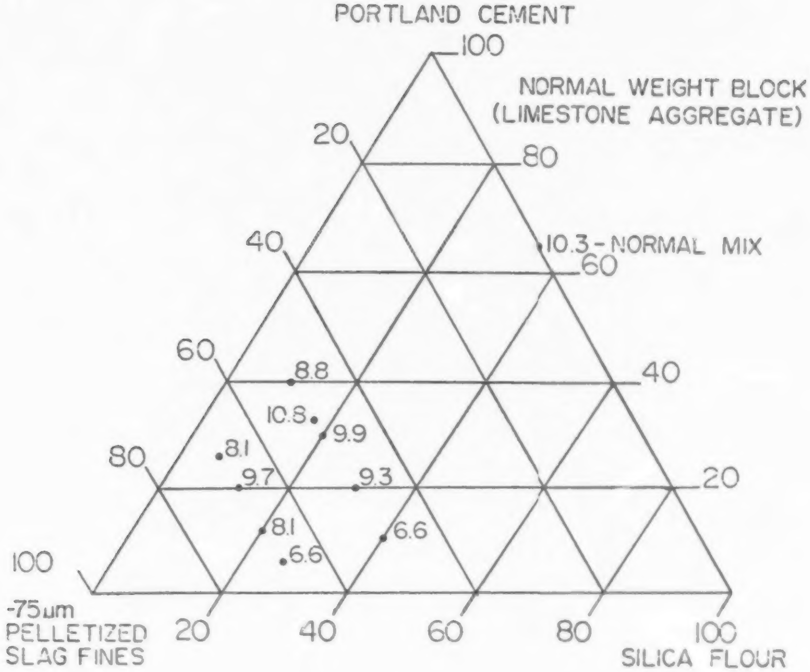

Fig. 5.6 — Compressive strengths of autoclaved blocks containing limestone aggregate (31)

200 x 200 x 400 mm (MPa, gross area)
CSA minimum = 6.9 MPa
Autoclave cycle 45 h total, 2.5 h at 180°C

ing aspect of these non-portland cement binders was much higher ratios of tensile (split tension) to compressive strength. In addition, in the field trials of autoclaved block described previously, blocks with a binder combination of 67% slag and 33% silica flour (no portland cement) developed 7.7-MPa strength (see Fig. 5.5).

In any case, it appears that the commonly accepted philosophy, that slag must be externally provided with an alkaline environment to hydrate, does not follow for these mixtures. Whereas the high-temperature autoclave-curing may activate the slag and slag–quartz mixtures by increasing the solubility of some of the alkaline components in the slag, and quartz may react more strongly than the amorphous silicates in the slag, no further tests were performed to confirm the mechanism.

6. CONCLUSIONS

The review of the published literature indicates that a high degree of vitrification is desirable to make slags suitable for cementitious end uses but, because of other influences, partially vitrified slags may possess similar reactivities to completely vitrified slags. If a determination of the degree of vitrification of a slag were to be made, it would be important to use a proper technique. Also, although several studies have shown that hydraulic potential generally increases with increased glass content, there is disagreement as to the sensitivity of glass content to strength. Few researchers have gone so far as to recommend a specific minimum glass content, but it appears that slags with as little as 30–65% glass contents are still suitable. Minimum glass contents are rarely found in standard specifications because it is generally agreed that performance (i.e., strength development) is a more reliable criterion for judging reactivity.

In spite of the existence of many chemical indices for the prediction of optimum hydraulicity, the effects of chemical composition are not clear, but it appears that slags over a wide range of compositions can be used for cementitious purposes. To produce a cement with uniform properties, consistency of chemical composition would be more important than the actual composition.

The usefulness of evaluating a slag in terms of its mineralogical composition is a point of controversy. However, knowledge of the types of crystalline minerals co-existing with the glass in quenched slags could be important in view of their effect on the chemical composition of the glass component.

Increasing the fineness of grinding improves the kinetics of slag reaction but energy considerations limit the practical range of grinding.

To develop strengths within a practical time frame, slags require external activation and are most often blended with portland cement. The hydration products of slags activated with portland cement are similar to those of portland cement alone, but the pore-size distribution of the hardened paste has been found to be finer and, consequently, the permeability should be reduced.

From the limited work on the autoclave-curing of slag, it appears that when activated by lime or portland cement without quartz, slag hydrates to tobermorite-like C-S-H and αC_2SH. Hydrogarnets, such as plazolite, have been found, but the shortest autoclave period in which this was noted was 12 h. With slags having a high MgO content, the aluminum serpentine $M_5AS_3H_4$ was found in several instances but again only at long curing cycle. Other studies have concluded that the MgO content of slags substituted into the C-S-H phase in a similar fashion to Al_2O_3. When ground quartz is introduced, more crystalline C-S-H or 11-Å tobermorite is formed at the expense of αC_2SH and CH, resulting in higher strength. As well, under autoclave conditions, slag can be activated by ground quartz alone.

It appears that the amount of slag used for cementitious purposes will continue to grow in North America, which should be enhanced by the developments of standard specifications by CSA and ASTM.

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CHAPTER 5

PROPERTIES OF FRESH AND HARDENED CONCRETE INCORPORATING GROUND, GRANULATED, BLAST-FURNACE SLAG

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1. INTRODUCTION

CANMET has recently become increasingly involved in research on cementitious materials, aimed at conserving both resources and energy. In particular, efforts have been directed at energy conservation by using less energy-intensive materials, such as fly ash, slag, and condensed silica fume. Of the concrete-making materials, cement is the most energy-intensive component, requiring about 4000 MJ/metric ton of product. The cost of energy to produce one metric ton of portland cement accounts for more than 40% of the total plant production cost (1–5). Thus, any attempt to reduce the amount of cement in concrete should result in considerable savings in energy. One of the most promising of the less energy-intensive materials for replacing cement is granulated slag, a by-product of the blast furnace in pig-iron production. The energy required to produce granulated slag is estimated at only 25 to 33% of that for portland cement (2,3,4,6). Considerable European data are available on the performance of blended slag cements which are produced by grinding the granulated blast-furnace slag and cement clinker together in a cement plant (7). However, only recently have data become available on the performance of concrete, in which ground, granulated, blast-furnace slag is added as a separate ingredient along with other mixture components at a concrete batch plant (8–11).

This chapter, which is the second of a three-part series, deals with the properties of fresh and hardened concrete incorporating ground, granulated blast-furnace slag as a separate ingredient at a concrete batch plant. It does not cover the performance of blended slag cements in concrete.

2. MIXTURE PROPORTIONS AND PROPERTIES OF FRESH CONCRETE

Mixture Proportions

The proportions of ground, granulated, or ground, pelletized, blast-furnace slag* to be used in concrete depend upon the job requirements. In normal ready-mixed concrete operations, in which the primary aim is to conserve cement, the usual proportions vary from 25 to 50% by weight of cement on a cement replacement basis. However, if the purpose is to enhance some aspect of concrete durability, e.g., sulphate resistance, then the slag content is at least 50% of the total cementitious material (12,13). As each slag has a unique chemical composition, glass content, and fineness, it is necessary to perform exploratory laboratory investigations with the cement, aggregates, and chemical admixtures to be used at a project, to determine the correct percentages of slag to be incorporated into the concrete. This aspect cannot be overemphasized.

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*Granulated slag implies that the slag is granulated by rapid-water quenching of the molten slag, whereas pelletized slag implies that the granulation is achieved by a pelletizing process. Hereafter, these are referred to either as granulated or pelletized slag, or only as slag when reference is made to both types.

The specific gravity of slags ranges from 2.85 to 2.95, compared to 3.15 for portland cements. Thus, a given replacement of cement by slag on a weight basis results in higher volume of paste in a concrete mixture. This result is of little consequence at lower percentages of cement replacement. If, however, 50 to 75% cement replacements are being considered, this will affect the rheology of the concrete mixtures, and may allow some increase in the volume of coarse aggregate to be used, especially in mixtures incorporating higher amounts of cement.

Time of Setting

The incorporation of slag as a replacement for portland cement in concrete normally results in increased setting time of concrete. Final setting time can be delayed up to several hours depending upon the ambient temperature, concrete temperature, and mixture proportions. At temperatures lower than 23°C, considerable retardation in setting time can be expected for slag concretes compared with control concrete, which has serious implications in winter concreting. At higher temperatures (>30°C), there is little or no change in setting time of slag concrete as compared to that of control concrete (13). Data by Hogan and Meusel (13) on initial and final setting times for concrete incorporating granulated slag are shown in Table 2.1.

CANMET (14) data on time of setting of concrete incorporating a pelletized slag and two different granulated slags are shown in Table 2.2.

In this study, at 25% cement replacement there was no significant increase in the initial setting time, whereas the increase in the final setting time ranged from 16 to 101 min. At 50% cement replacement, the increase in the initial setting time of the concretes ranged from 17 to 80 min, whereas the increases in the final setting time ranged from 93 to 192 min.

Bleeding

Few published data are available on the bleeding of slag concretes. Slags are generally ground to a higher fineness than normal portland cement and, therefore, a given mass of slag has a higher surface area than the corresponding mass of portland cement. As the bleeding of concrete is governed by the ratio of the surface area of solids to the volume of water, in all likelihood the bleeding of slag concrete will be lower than that of the corresponding control concrete. The slags now available in Canada and the USA have finenesses, as measured by the Blaine surface area method, greater than 4000 cm^2/g compared with that of about 3000 cm^2/g for portland cement. Thus, in concrete in which a given mass of portland cement is replaced by an equivalent mass of slag, bleeding should not be a problem.

Table 2.1 — Data on time of setting for air-entrained concrete incorporating granulated slag*

Properties	Slag content, %				Slag content, %			
	Control, no slag	40	50	65	Control, no slag	40	50	65
Water/(cement + slag)	0.40	0.40	0.40	0.40	0.55	0.55	0.55	0.55
Cement factor (cement and slag), kg/m³	413	435	419	408	272	290	245	301
Fine aggregate/coarse aggregate	33/67	33/67	33/67	33/67	46/54	46/54	46/54	46/54
Air content, %	5.4	3.4	4.5	5.0	4.3	3.5	6.0	4.9
Unit weight, kg/m³	2330	2350	2320	2310	2345	2355	2310	2295
Slump, mm	75	75	95	90	70	15	50	75
Air-entraining admixture mL/kg cement	4.4	4.4	9.0	9.5	8.4	4.6	8.2	8.2
Initial set at 21.1°C (70°F), h:min	4:06	4:02	4:31	4:30	4:32	5:02	5:10	5:21
Final set at 21.1°C (70°F), h:min	5:34	5:40	6:29	7:04	7:03	6:40	8:10	8:09
Initial set at 32.2°C (90°F), h:min	3:30	—	3:45	—	—	—	—	—
Final set at 32.2°C (90°F), h:min	4:10	—	4:50	—	—	—	—	—

* From reference (13).

Table 2.2 — Bleeding and setting-time of slag concrete: comparative data on three different slags*

Mixture no.	Type and source of slag	Blaine fineness of slag, cm²/g	Cement replacement by slag, %	W/(C+S)	Setting time, h:min		Total bleeding water cm³/cm² × 10⁻²
					Initial	Final	
1 C	—	—	0	0.50	4:56	6:27	4.16
2 ST	Pelletized (Canada)	4200	25	0.50	4:49	7:15	4.29
3 AT	Granulated (USA)	5400	25	0.50	4:23	6:43	3.08
4 AL	Granulated (Canada)**	3700	25	0.50	4:54	7:52	6.11
5 AL	Granulated (Canada)**	4600	25	0.50	4:49	7:20	5.67
6 AL	Granulated (Canada)**	6080	25	0.50	5:30	8:08	5.00
7 ST	Pelletized (Canada)	4200	50	0.50	5:54	9:32	4.13
8 AT	Granulated (USA)	5400	50	0.50	5:13	8:00	3.33
9 AL	Granulated (Canada)**	3700	50	0.50	6:06	9:39	9.50
10 AL	Granulated (Canada)**	4600	50	0.50	—	—	6.20
11 AL	Granulated (Canada)**	6080	50	0.50	6:16	9:37	2.78

* From reference (14).

** Same source but ground to different finenesses.

Note: Cement type: ASTM Type I, C.A.: crushed limestone 19-mm max size, F.A.: natural sand; A.E.A.: sulphonated hydrocarbon type.

In the CANMET study already discussed (14), bleeding rate and total bleeding water were also determined on concrete incorporating one pelletized and two granulated slags at two cement replacement levels. The ratio of water to cementitious materials was kept constant (see Table 2.2).

The data presented in Figures 2.1 and 2.2, and in Table 2.2 show that, in general, the total bleeding water was lowest for the concrete made with a granulated slag from the USA and was highest for the concrete made with a granulated slag from a Canadian source. The difference is probably due to the different finenesses of the slags used; the Blaine fineness for the former slag was 5400 cm^2/g whereas the value for the latter was 3700 cm^2/g.

Dosage of Air-Entraining Admixtures

The dosage requirement of an air-entraining admixture to entrain a given volume of air in slag concrete increases with increasing amounts of slag. The increased demand for the admixture is, once again, probably due to the higher total surface area of the slag particles as compared with that of the portland cement particles. For example, in one CANMET investigation (15), the admixture dosage needed to entrain about 5% air increased from 177 mL/m^3 for the control concrete to 562 mL/m^3 for the concrete mixture incorporating 65% pelletized slag. The water-to-(cement + slag) ratio was 0.30. At higher water-to-(cement + slag) ratios, the increase was not as marked as that at lower water-to-(cement + slag) ratios (Fig. 2.3). Similar results have been reported for air-entrained and superplasticized concrete incorporating pelletized slag (Fig. 2.4).

Dosage Rate of Superplasticizers

Limited investigations at CANMET (15) have shown that superplasticizers (high-range water-reducing admixtures) are as effective in slag concrete as they are in normal portland cement concrete, in spite of different dosage requirements. In one investigation dealing with the pelletized slag, the dosage required for a melamine formaldehyde, sulphonated-type superplasticizer decreased from 1.3% by weight of cementitious material for the control concrete to 1.0% for the concrete mixture incorporating 65% slag (15). This finding may or may not be true for concretes incorporating other types of slags, or superplasticizers, or both.

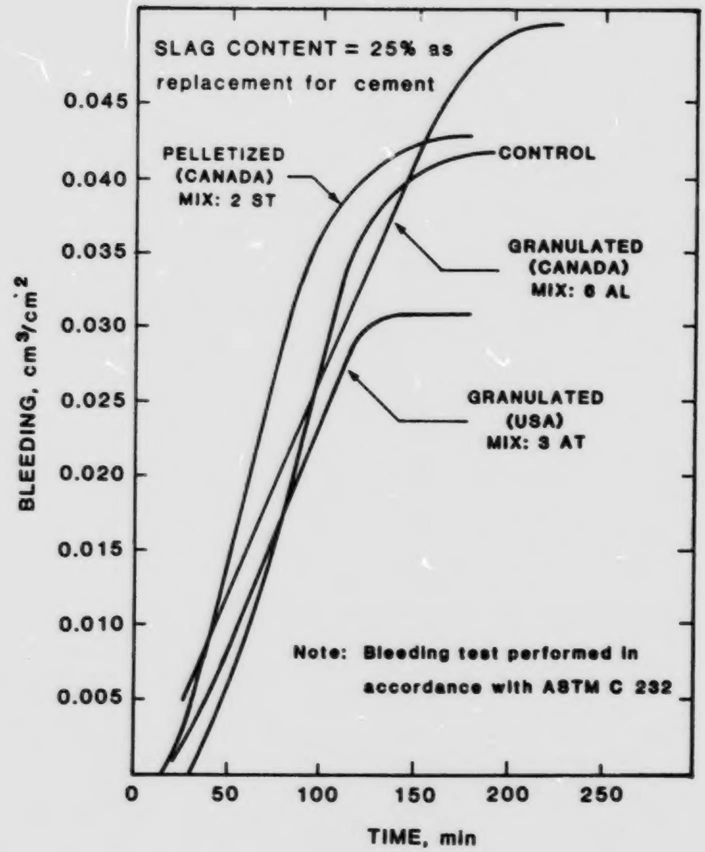

Fig. 2.1 — Comparative data on rate of bleeding and bleeding of concrete incorporating slags at 25% cement replacement level (14)

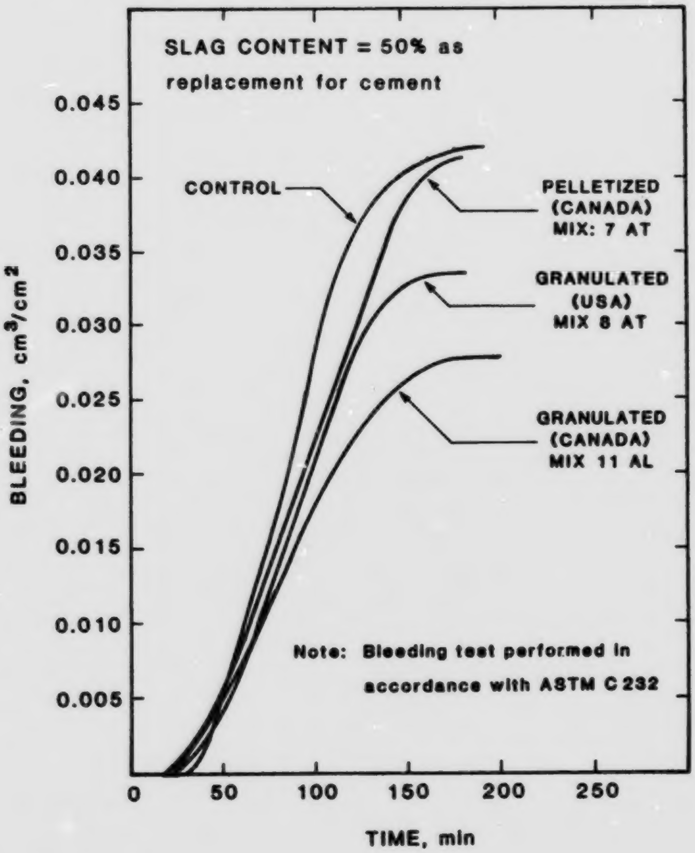

Fig. 2.2 — Comparative data on rate of bleeding and bleeding of concrete incorporating slags at 50% cement replacement levels (14)

Slump and Workability

Meusel and Rose (16) have reported that as the granulated slag portion of the cementitious material in the concrete is increased there is an increase in slump. Exceptions have been reported for pelletized slag concrete (15). Though there are no universally accepted tests for determining workability of concrete, both Fulton (9) and Wood (17) have reported that workability of slag concretes shows improved characteristics, which probably is because of the increased paste content of the concrete mixture. It has been reported (9) that concrete incorporating granulated slag requires less vibrating effort during placing operations in the field. This observed phenomenon is not well documented and needs well-designed field experiments to confirm it.

Rates of Slump Loss and Entrained Air Loss

Meusel and Rose (16) have shown that the rate of slump loss of concrete incorporating granulated slag at 50% cement replacement was comparable to that of the control concrete.

From recent CANMET investigations, data on the rate of slump loss for concrete incorporating granulated slag are shown in Figure 2.5. The concrete had a ratio of water to cementitious materials of 0.50 and incorporated granulated slag at 50% cement replacement. Both the slag concrete and the control concrete had an initial slump of about 45 mm.

During the initial 60 min, the control concrete had lost more slump than the slag concrete; however, at the end of 85 min both concretes had a slump of only 5 mm, showing a loss of about 40 mm in each case. It is believed that the rate of slump loss will vary with the initial slump and water-to-cementitious materials ratio of concrete.

The rate of loss of entrained air with time is shown in Figure 2.6 for both control and granulated slag concretes. The rate of loss of entrained air was somewhat similar for both types of concretes, and the total loss of entrained air during the first 85 min was 2.5% for the control concrete and 2.7% for the granulated slag concrete at 50% cement replacement. For granulated slag concrete, the rate of loss measurements were continued for another 80 min, at the end of which the additional loss of air was only 0.6%. The significance of these data is that when considerable delay is expected in mixing and placing concrete, the initial air content would have to be increased to ensure satisfactory entrained air in concretes at the time of placing.

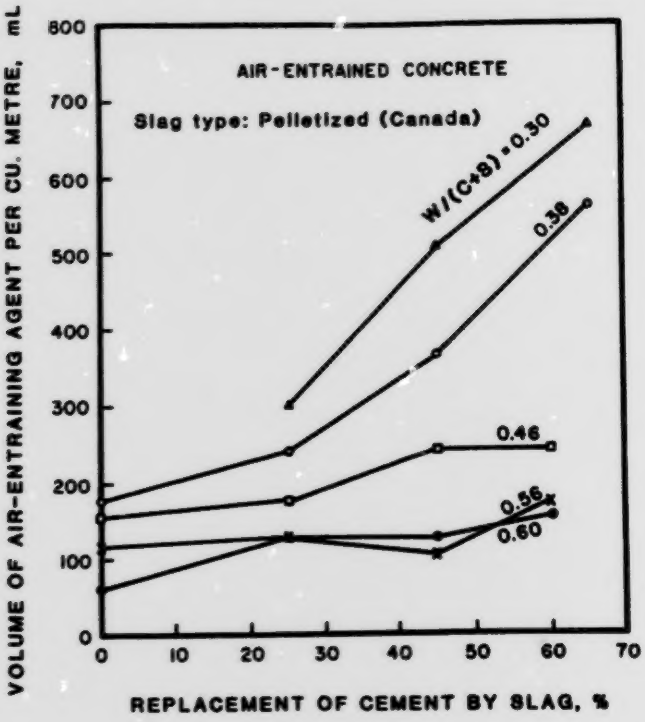

Fig. 2.3 — Dosage of air-entraining agent versus pelletized slag content: air-entrained concrete (15)

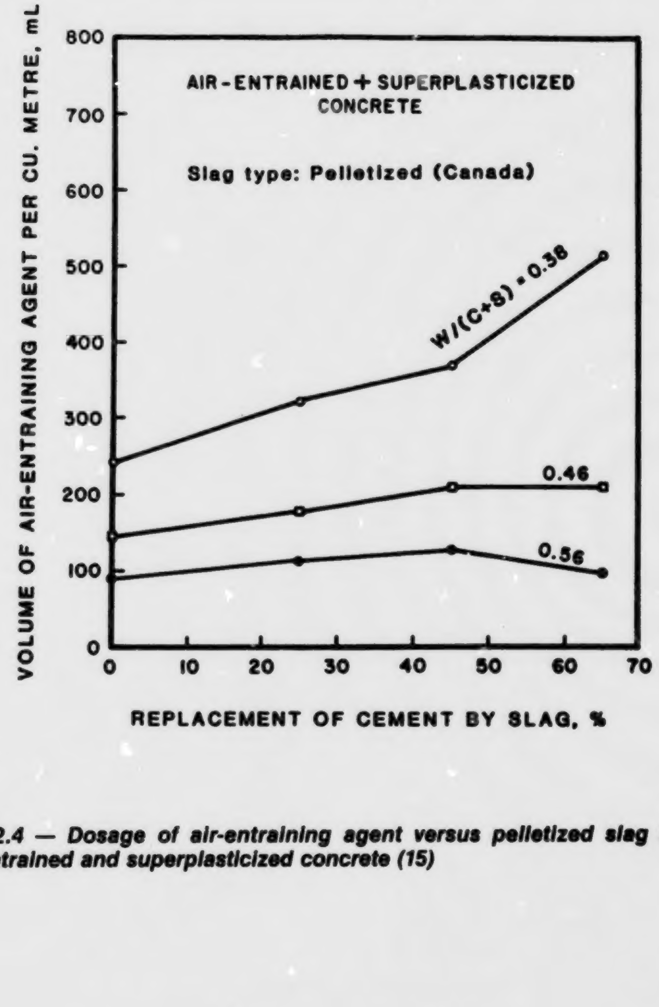

Fig. 2.4 — Dosage of air-entraining agent versus pelletized slag content: air-entrained and superplasticized concrete (15)

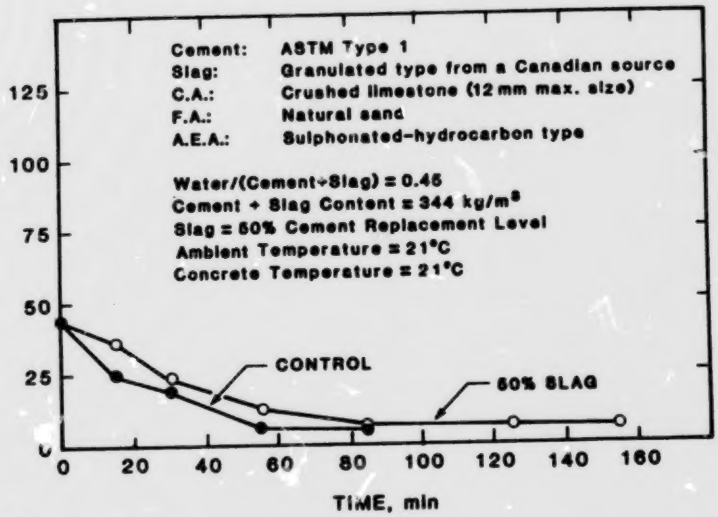

Fig. 2.5 — Rate of slump loss with time for concrete incorporating granulated slag at 50% cement replacement level (From unpublished CANMET data)

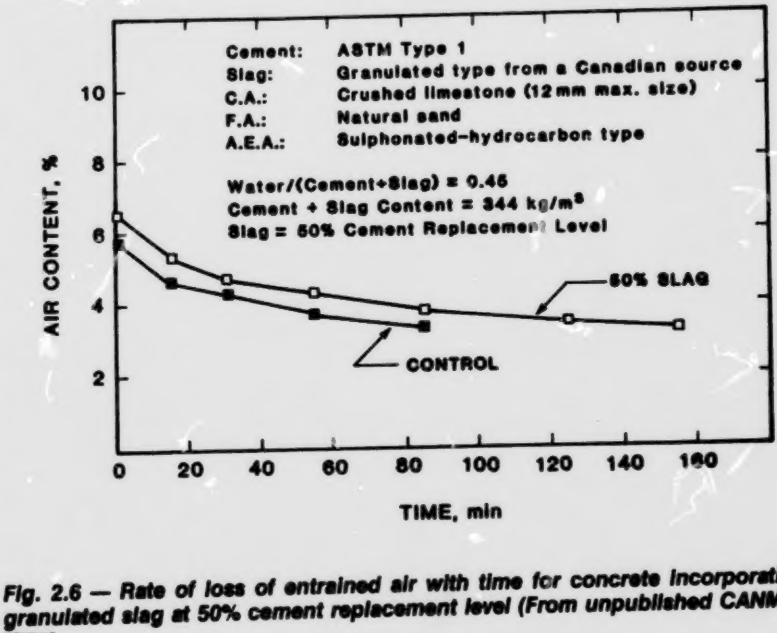

Fig. 2.6 — Rate of loss of entrained air with time for concrete incorporating granulated slag at 50% cement replacement level (From unpublished CANMET data)

3. PROPERTIES OF HARDENED CONCRETE

Colour

Concrete incorporating slags is generally lighter in colour than normal portland cement concrete, due to the lighter colour of slags. When concrete is tested in compression or flexure, the interior of the broken specimens exhibit deep blue-green colour. After sufficient exposure to air, the colour disappears. The degree of colour, which results from the reaction of sulphides in the slag with other compounds in cement, depends upon the percentage of slag used, curing conditions, and the rate of oxidation.

Curing

The rate and degree of hydration of cement paste, and consequently its strength, are affected significantly by lack of proper curing. This effect becomes more pronounced when the paste incorporates high percentages of slag, because of the slow formation of strength-producing hydrates. Thus, to ensure proper strength and durability of concretes incorporating high percentages of slag (>30%), it is important that they are given more curing than those concretes without slag (9). Such extended curing is especially important during winter concreting in Canada and the northern United States. The length of increase in curing time would depend upon the ambient temperature, the concrete temperature, the type and amount of cement used, and the percentage of cement replacement.

Compressive Strength

The compressive strength development of slag concrete depends primarily upon the type, fineness, activity index, and the proportions of slag used in concrete mixtures. Other factors that affect the performance of slag in concrete are the water-to-cementitious materials ratio and the type of cement used. In general, the strength development of concrete incorporating slags is slow at one to five days compared with that of the control concrete. Between 7 and 28 days, the strength approaches that of the control concrete and beyond this period, the strength of slag concrete exceeds the strength of control concrete. Fig. 3.1 and 3.2 show compressive strength development with age for granulated slag concrete for water-to-(cement + slag) ratios of 0.40 and 0.55. It is noted that the highest strength gain at 28 days was for concrete with the slag content at 40% cement replacement. The strength versus age relationships for concrete incorporating pelletized slag are shown in Figures 3.3 to 3.9, both for air-entrained, and air-entrained and superplasticized concretes. The data presented in the figures indicate that, for the pelletized slag investigated, the compressive strength of the slag concrete is lower than that of the control concrete, particularly at early ages, and this is markedly so for the concretes with low water-to-(cement + slag) ratios. This result is contrary to the general trends mentioned previously and may or may not be true for pelletized slags of other sources. It is important to perform exploratory laboratory investigations for each type of slag to develop age versus strength relationships.

With ageing, the strength of slag concretes with high water-to-cementitious materials ratio either approaches or exceeds that of the control concrete (see Figures 3.3, 3.4, 3.7, and 3.8), whereas, the strength of slag concretes with low water-to-cementitious materials ratio, regardless of age, remains lower than the control concrete strength (see Figures 3.5, 3.6, and 3.9). Similar trends have been reported by Fulton (9) and Meusel and Rose (16) for concrete incorporating granulated slag.

Comparative data on properties of slag concretes, both in the fresh and hardened state, using slags from three different sources in Canada and the USA are shown in Tables 3.1 and 3.2. At 25 and 50% cement replacement, the seven-day compressive strength of the control concrete exceeds that of the slag concrete for two of the slags used. In the case of the third slag, the strengths are comparable. However, at 28 and 91 days, the trend reverses, and generally, the strengths of the slag concretes exceed that of the control concrete.

Malhotra et al. (18) have reported investigations in which small amounts of condensed silica fume have been added to pelletized slag concrete to increase the early-age strength. Figures 3.10 to 3.12 illustrate the strength development of concrete from 1 day to 180 days. The authors concluded:

— "The low early-age strength of portland cement concrete incorporating blast furnace slag can be increased by the incorporation of condensed silica fume. The gain in strength is, in general, directly proportional to the percentage of the fume used.

— "At three days, the increase in strength is generally marginal, especially for concrete with high W/(C + BFS). However, at the age of 14 days and beyond, with minor exceptions, the loss in compressive strength of concrete due to the incorporation of BFS can be fully compensated for with a given percentage of condensed silica fume, regardless of the W/(C + BFS). This is also true for the flexural strength.

— "The continuing increase in strength at 56, 91 and 180 days of the concrete incorporating BFS and condensed silica fume indicates that sufficient lime (liberated during the hydration of portland cement) is present at these ages for the cementitious reaction to continue."

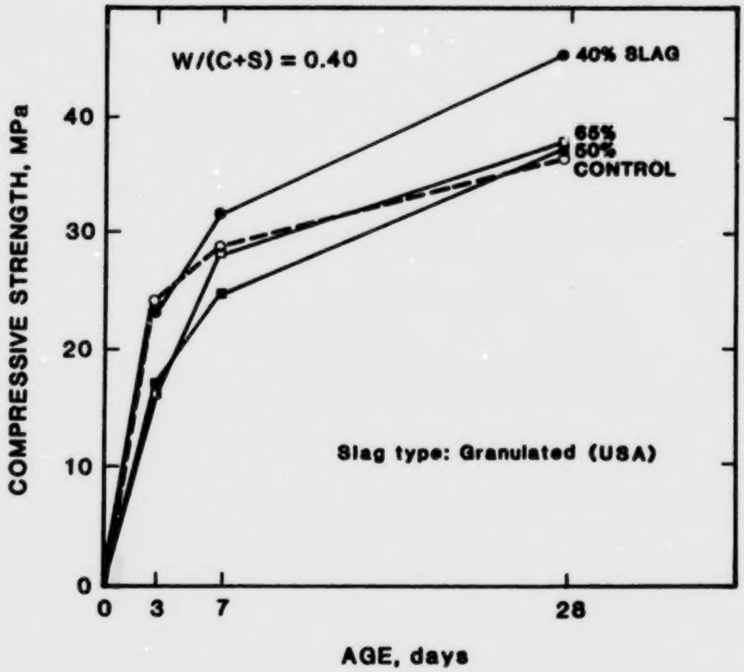

Fig. 3.1 — Age versus compressive strength relationship for air-entrained concrete: W/(C+S) = 0.40 (13)

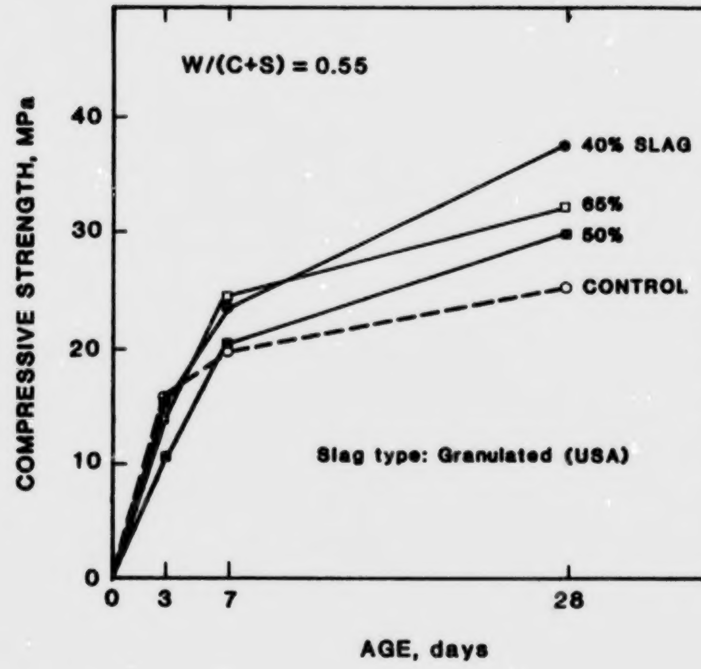

Fig. 3.2 — Age versus compressive strength relationship for air-entrained concrete: W/(C+S) = 0.55 (13)

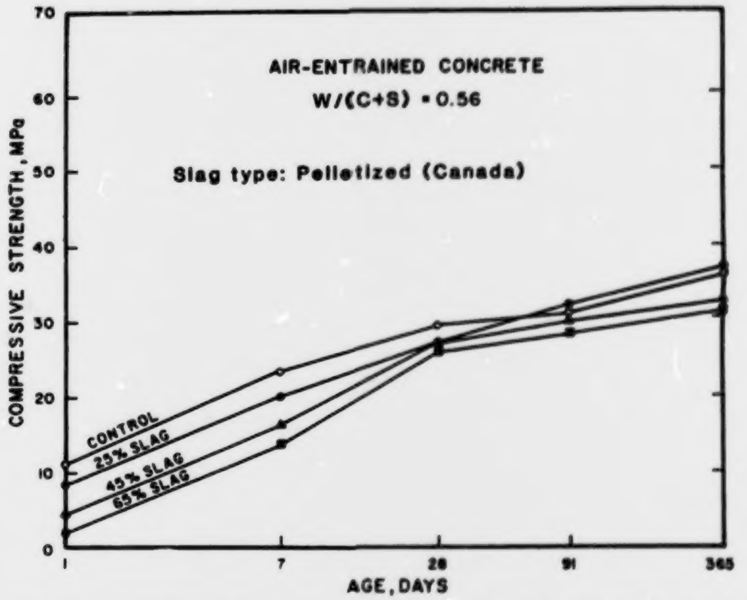

Fig. 3.3 — Age versus compressive strength relationship for air-entrained concrete: W/(C+S) = 0.56 (15)

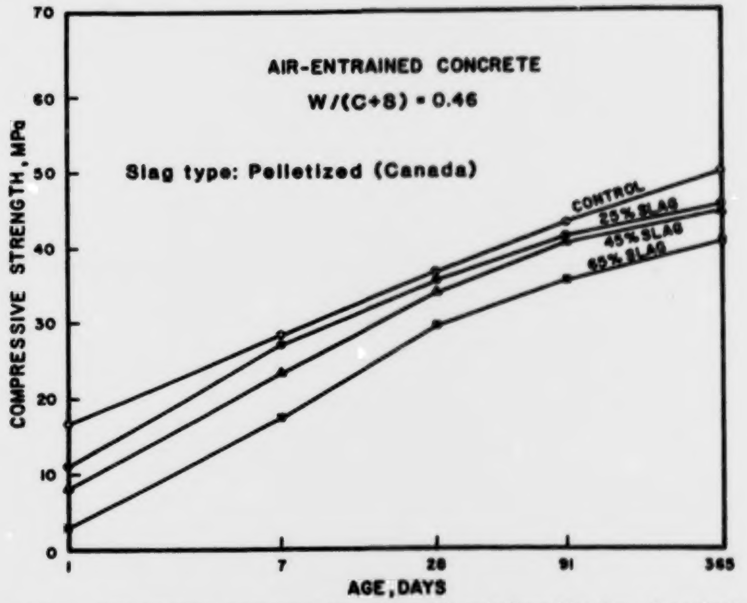

Fig. 3.4 — Age versus compressive strength relationship for air-entrained concrete: W/(C+S) = 0.46 (15)

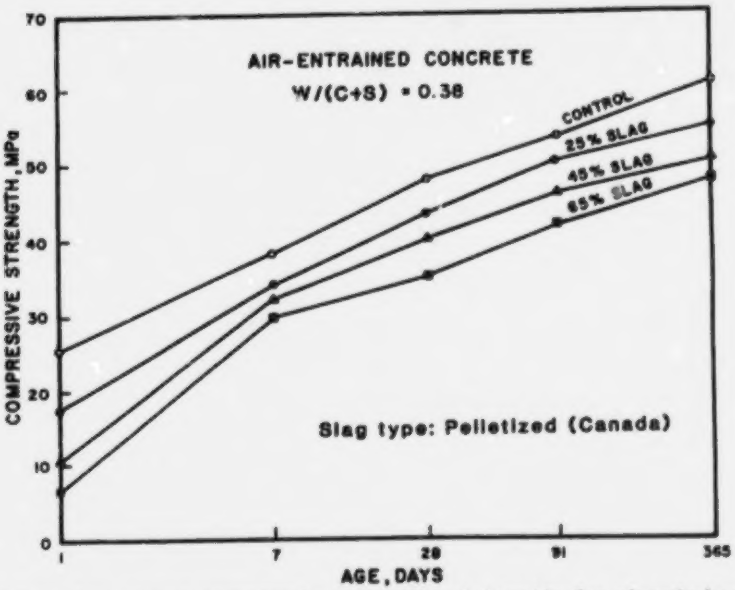

Fig. 3.5 — Age versus compressive strength relationship for air-entrained concrete: W/(C + S) = 0.35 (15)

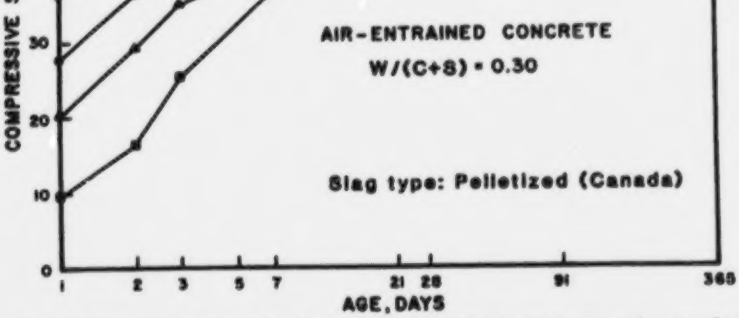

Fig. 3.6 — Age versus compressive strength relationship for air-entrained concrete: W/(C + S) = 0.30 (15)

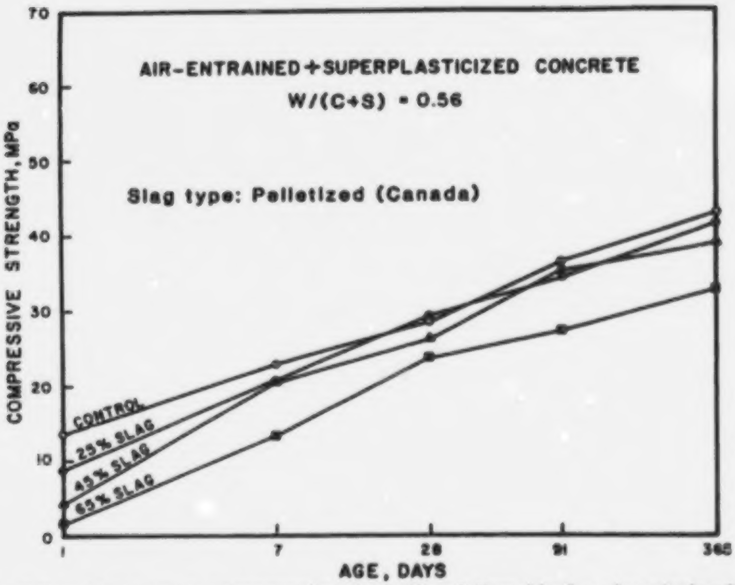

Fig. 3.7 — Age versus compressive strength relationship for air-entrained and superplasticized concrete: W/(C+S) = 0.56 (15)

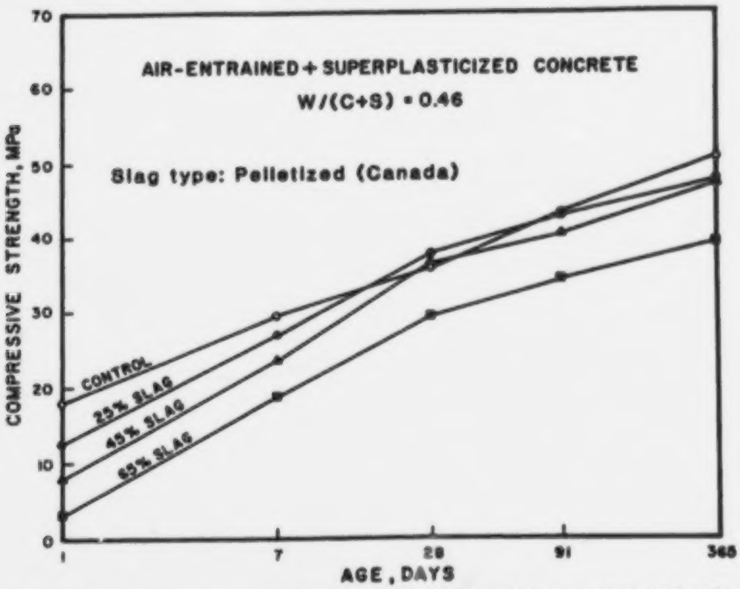

Fig. 3.8 — Age versus compressive strength relationship for air-entrained and superplasticized concrete: W/(C+S) = 0.46 (15)

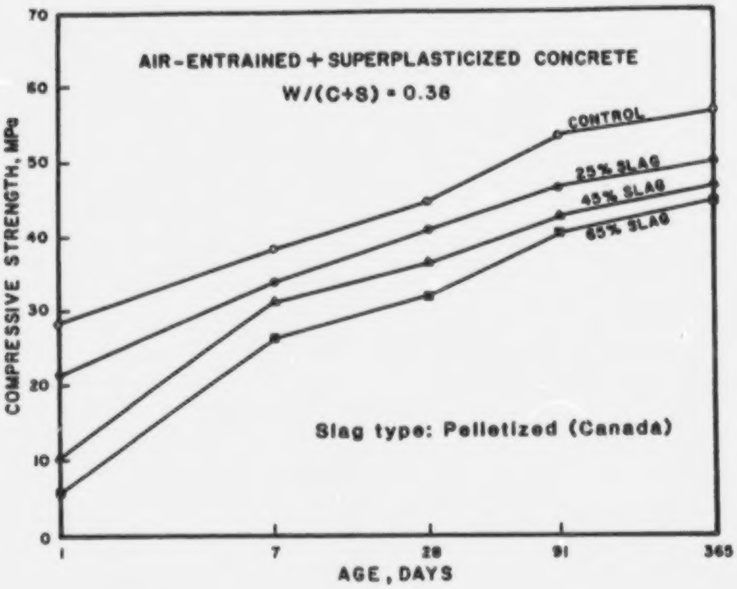

Fig. 3.9 — Age versus compressive strength relationship for air-entrained and superplasticized concrete: W/(C+S) = 0.38 (15)

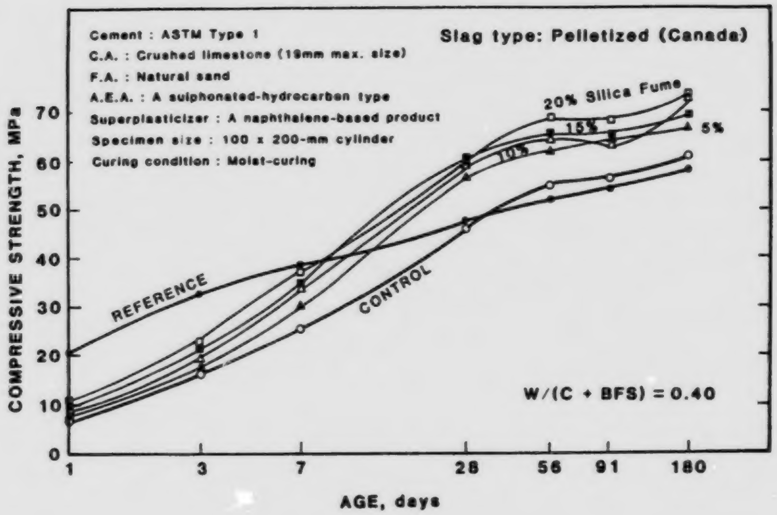

Fig. 3.10 — Age versus compressive strength relationship for concrete incorporating condensed silica fume and pelletized slag: W/(C+BFS) = 0.40 (18)

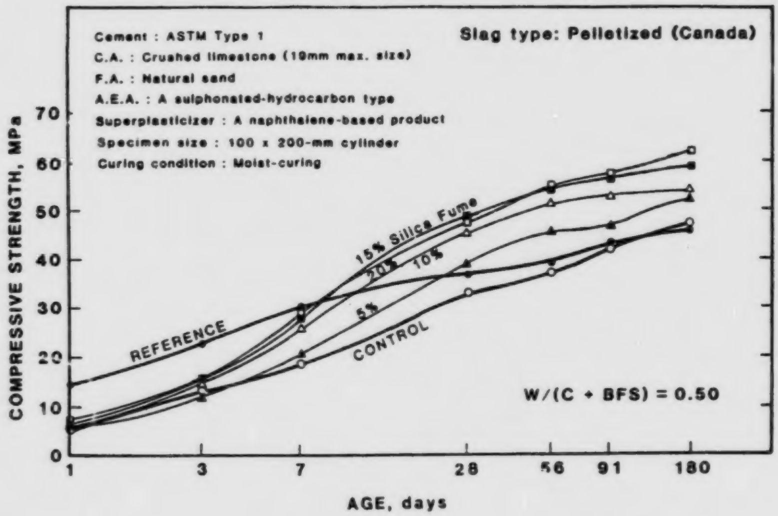

Fig. 3.11 — Age versus compressive strength relationship for concrete incorporating condensed silica fume and pelletized slag: W/(C+BFS) = 0.50 (18)

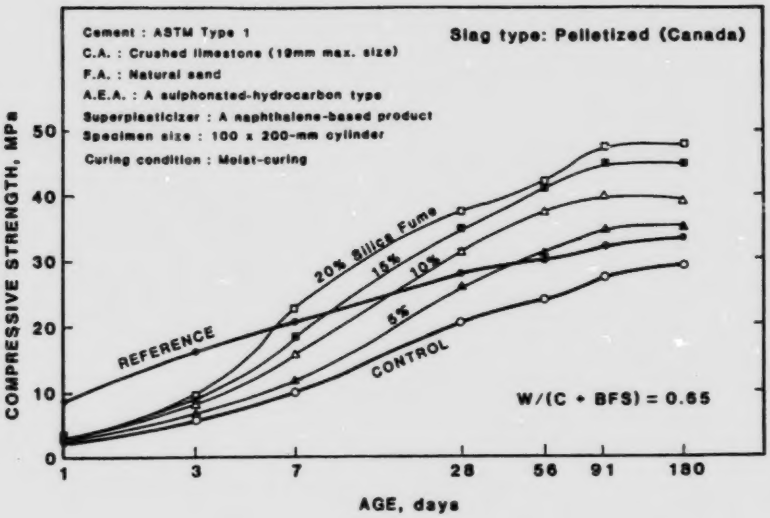

Fig. 3.12 — Age versus compressive strength relationship for concrete incorporating condensed silica fume and pelletized slag: W(C + BFS) = 0.65 (18)

Table 3.1 — Mixture proportions and properties of fresh concrete: comparative data on three different slags*

					Mixture proportions, kg/m³						Properties of fresh concrete			
Mixture no.	Type and source of slag	Blaine fineness of slag, cm²/g	Cement replacement by slag, %	W/(C+S)	Water	Cement	Slag	F.A. (SSD)	C.A. (SSD)	A.E.A. mL/m³	Slump, mm	Unit weight, kg/m³	Air content, %	Temp, °C
1 C	—	—	0	0.50	162	323	—	720	1077	108	110	2280	6.7	21
2 ST	Pelletized (Canada)	4200	25	0.50	168	252	84	715	1069	122	120	2290	6.1	23
3 AT	Granulated (USA)	5400	25	0.50	167	250	84	713	1066	122	120	2280	6.5	23
4 AL	Granulated (Canada)**	3700	25	0.50	167	251	84	713	1066	92	140	2280	6.0	21
5 AL	Granulated (Canada)**	4600	25	0.50	167	250	84	710	1063	97	135	2275	6.7	23
6 AL	Granulated (Canada)**	6080	25	0.50	166	249	83	707	1057	106	135	2260	6.9	20
7 ST	Pelletized (Canada)	4200	50	0.50	166	166	166	707	1056	145	120	2260	6.7	22
8 AT	Granulated (USA)	5400	50	0.50	169	169	169	716	1071	122	95	2295	6.0	24
9 AL	Granulated (Canada)**	3700	50	0.50	166	166	166	707	1057	96	135	2260	6.8	23
10 AL	Granulated (Canada)**	4600	50	0.50	168	168	168	713	1066	93	120	2280	6.2	—
11 AL	Granulated (Canada)**	6080	50	0.50	166	166	166	703	1051	129	115	2250	6.9	21

* From reference (14).

** Same source but ground to different finenesses.

Note: Cement type: ASTM Type I

C.A. : crushed limestone 19-mm max size

F.A. : natural sand

A.E.A. : sulphonated hydrocarbon type.

Table 3.2 — Compressive and flexural strength test results: comparative data on three different slags*

Mixture no.	Source and type of slag	Blaine fineness of slag, cm²/g	Cement replacement by slag, %	W/(C+S)	Compressive strength on 150x300-mm cylinders, MPa					Flexural strength on 75x75x400-mm prisms, MPa	
					3-day	7-day	28-day	91-day	365-day	7-day	14-day
1 C	—	—	0	0.50	17.8	21.1	26.9	31.6	35.0	3.8	4.8
2 ST	Pelletized (Canada)	4200	25	0.50	16.0	19.9	28.6	34.1	36.6	4.0	5.3
3 AT	Granulated (USA)	5400	25	0.50	17.6	22.9	29.8	33.9	38.1	4.6	5.1
4 AL	Granulated (Canada)**	3700	25	0.50	14.9	18.5	25.4	31.0	33.1	3.9	5.4
5 AL	Granulated (Canada)**	4600	25	0.50	13.8	18.8	26.0	30.2	32.9	4.1	4.8
6 AL	Granulated (Canada)**	6080	25	0.50	15.6	21.0	28.2	31.5	35.8	4.4	5.0
7 ST	Pelletized (Canada)	4200	50	0.50	9.0	14.1	25.4	29.5	33.8	3.2	5.2
8 AT	Granulated (USA)	5400	50	0.50	14.9	22.7	33.6	37.6	40.4	4.3	5.7
9 AL	Granulated (Canada)**	3700	50	0.50	10.4	15.6	24.7	29.1	33.0	3.7	5.0
10 AL	Granulated (Canada)**	4600	50	0.50	9.5	15.9	25.5	29.8	34.3	3.6	5.1
11 AL	Granulated (Canada)**	6080	50	0.50	12.2	20.7	30.1	32.9	37.2	4.3	5.2

* From reference (14).

** Same source but ground to different finenesses.

Note: Cement type: ASTM Type I
C.A. : crushed limestone 19-mm max size
F.A. : natural sand
A.E.A. : sulphonated hydrocarbon type.

Flexural Strength

In general, at seven days and beyond, the flexural strength of concrete incorporating slag is comparable to, or greater than, the corresponding strength of control concrete (Figs. 3.13 to 3.17); however, in one instance, the reverse has been reported for water-to-(cement + slag) ratio of 0.38 (see Fig. 3.15). The increased flexural strength of slag concrete is probably due to the stronger bonds in the cement/slag/aggregate system because of the shape and surface texture of the slag particles.

Comparative data on flexural strengths of concretes incorporating three different types of slags from Canada and the USA are shown in Table 3.2. In general, regardless of the percentage replacement and the type of slag used, the flexural strengths of the slag concretes exceeded that of the control concrete at both 7 and 14 days.

Modulus of Elasticity

According to Stutterheim (19), at the same strength level, there is little, if any, difference between the modulus of elasticity of the control concrete and of that containing a granulated slag of South African origin. No published data are available on modulus of elasticity of slags currently available in North America. Investigations performed by Nakamura et al. (20) on a Japanese slag showed no significant difference between the values of modulus of elasticity of concrete incorporating granulated slag and that of the control concrete.

Table 3.3 shows modulus of elasticity data by Wainwright and Tolloczko (21) on concrete incorporating a slag from the United Kingdom. At early ages and at high percentages of slag, the slag concretes show lower modulus in relation to the control concrete.

Table 3.3 — Static modulus of elasticity*

Slag content					
0%		50%		70%	
Age, days	E, GPa	Age, days	E, GPa	Age, days	E, GPa
1	26.5	1	17.0	1	6.5
2	31.5	2	20.0	2	14.0
4	34.0	3	25.0	3	18.5
7	36.0	7	28.5	7	25.5
31	38.5	28	37.0	28	32.0
56	39.5	56	39.0	56	35.0
171	41.0	165	42.0	174	39.5

* From reference (21).

Note: Concretes were proportioned to have minimum cube compressive strength of 45 MPa at 28 days.

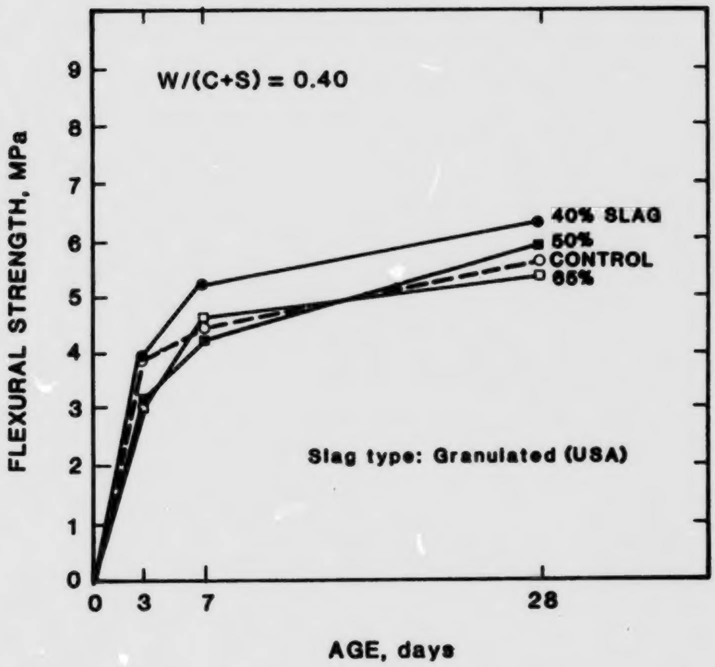

Fig. 3.13 — Age versus flexural strength relationship for air-entrained concrete: W/(C+S) = 0.40 (13)

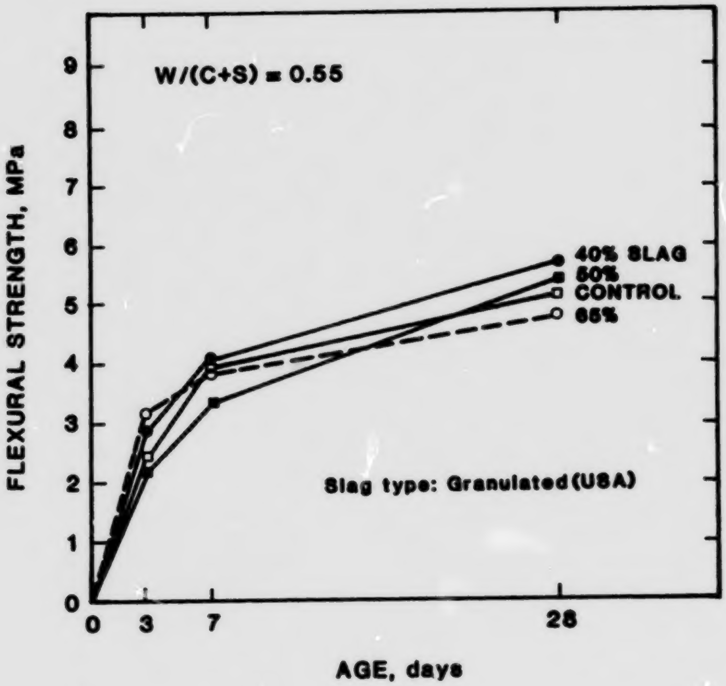

Fig. 3.14 — Age versus flexural strength relationship for air-entrained concrete: W/(C+S) = 0.55 (13)

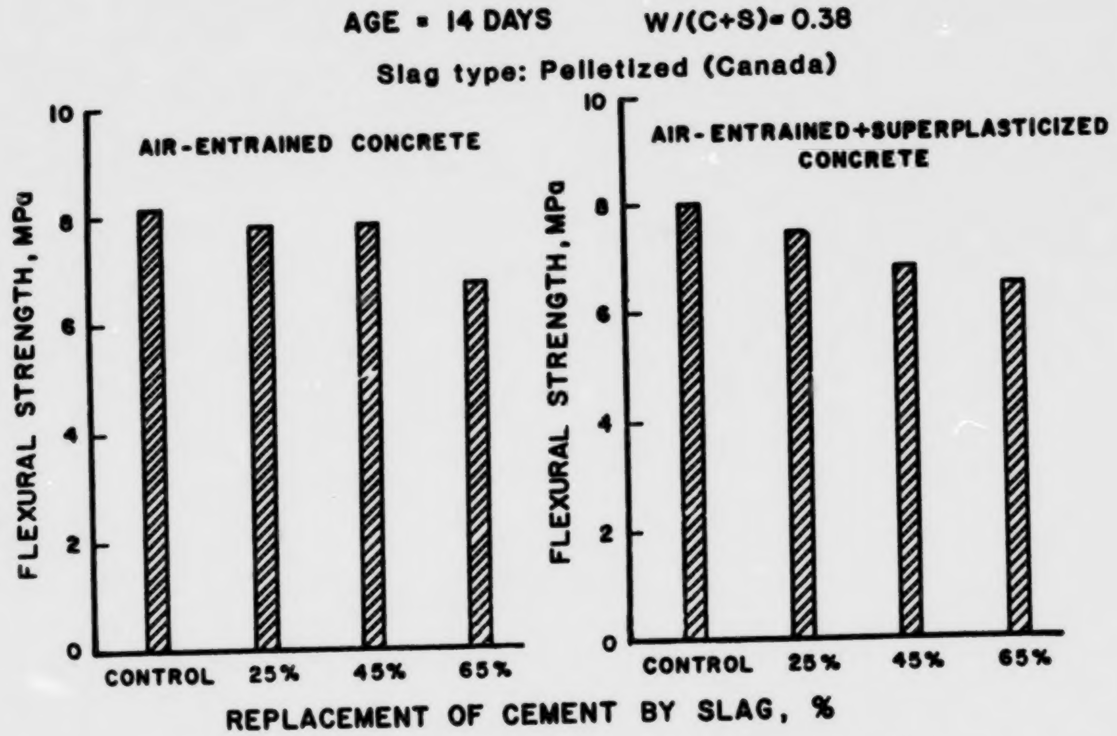

Fig. 3.15 — Flexural strength of air-entrained concrete at 14 days: W/(C+S) = 0.38 (15)

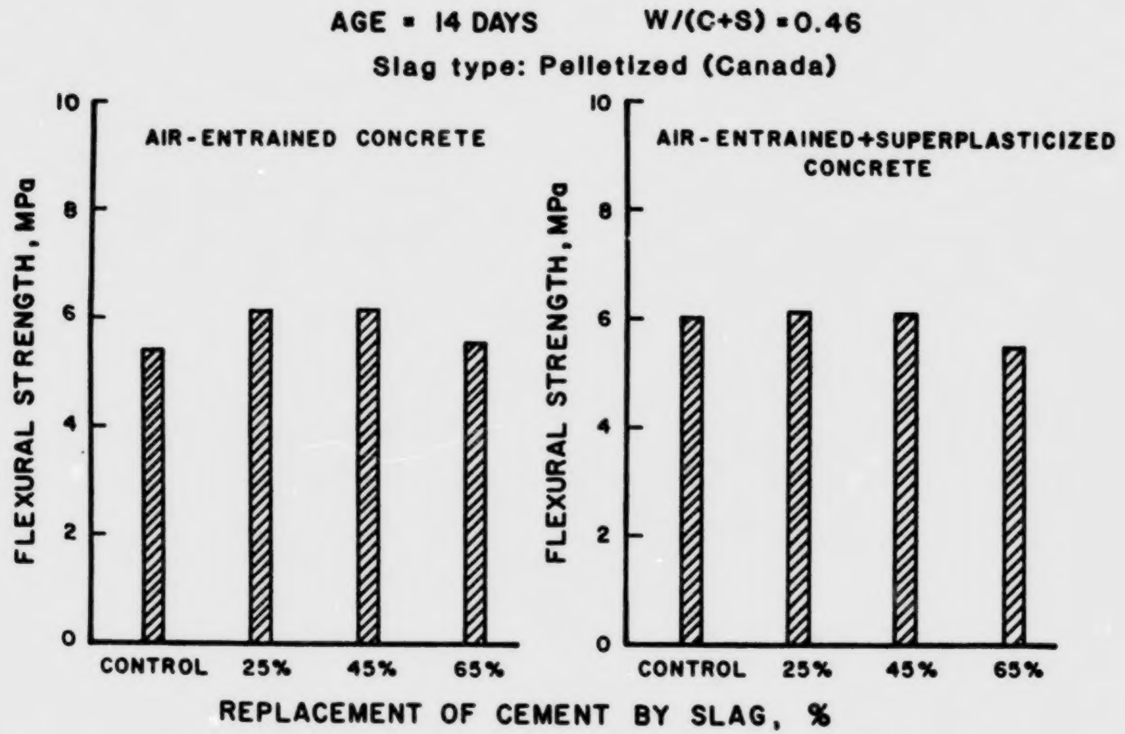

Fig. 3.16 — Flexural strength of air-entrained concrete at 14 days: W/(C+S) = 0.46 (15)

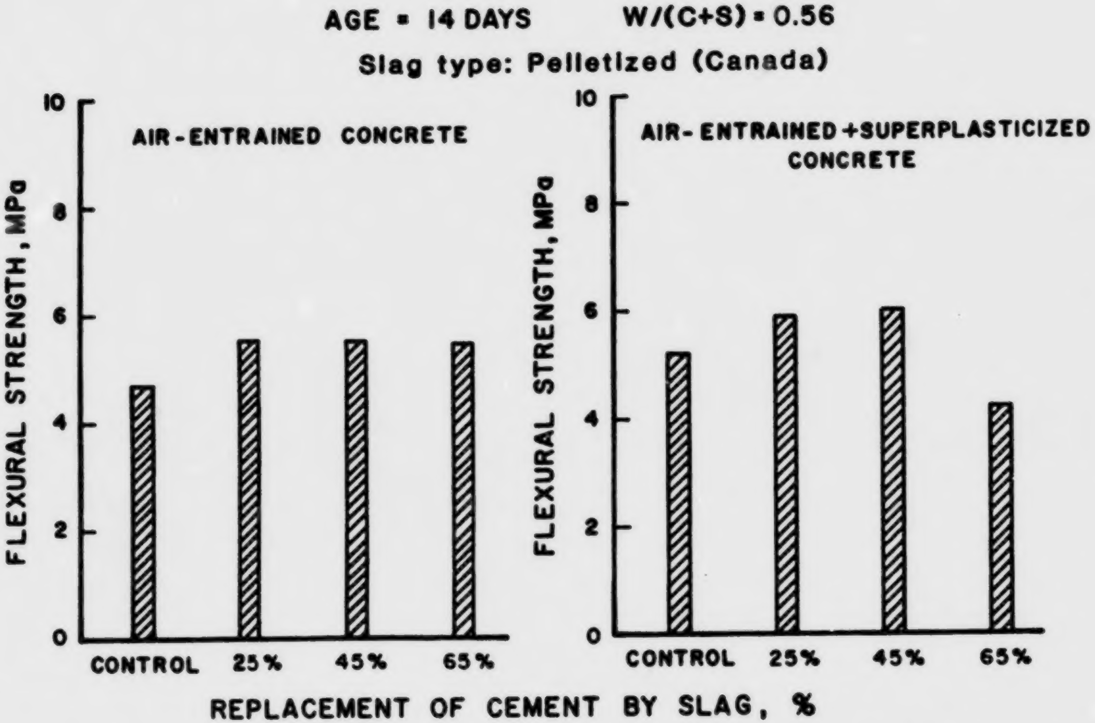

Fig. 3.17 — Flexural strength of air-entrained concrete at 14 days: W/(C+S) = 0.56 (15)

Drying Shrinkage

Hogan and Meusel (13) have shown that drying shrinkage of concrete incorporating granulated slag is more than that of the control concrete (Figs. 3.18 and 3.19). The increase in shrinkage is attributed to increased paste volume in the concrete when the slag is used as replacement for portland cement on an equal weight basis, because of the lower specific gravity of the slag. This finding may or may not be true for other slags and further research is needed to confirm this. Fulton (9) has suggested that the shrinkage of concrete incorporating granulated slag can be reduced by taking advantage of improved workability to increase the aggregate-to-cement ratio, or to reduce the water-to-cement ratio of concrete.

Creep

There are few published data on creep of concrete incorporating currently available North American slags. The available data from South Africa and Japan are conflicting (9). This conflict is due primarily to the finenesses of slags used, methods of tests, age of testing, humidity conditions, and the stress–strength ratio employed. For example, it has been shown that fineness of cement affects significantly the creep strains (9). Bamforth (22) has reported limited data on creep strains on concretes with and without fly ash and granulated slags, loaded to a constant stress–strength ratio of 0.25 (Fig. 3.20). He found that for concretes loaded at an age greater than 24 h, the effects of fly ash and slag were to reduce significantly the magnitude of the creep.

Neville and Brooks (23) have shown that when creep tests are performed at ordinary room temperature and humidity conditions (i.e., 20°C and 60% RH) on test specimens which have been loaded after moist-curing for 28 days, the total creep of the concrete incorporating a slag from a British source was greater than that of the control concrete, though not significantly so (Fig. 3.21). The rationale for this finding may be that under such test conditions the rate of gain of strength of the slag concrete is lower than that of the control concrete.

Neville and Brooks have also shown that under conditions of no moisture loss, the basic creep of concrete containing slag at 50% cement replacement level was about 42% lower than that of the control concrete (Fig. 3.22). The authors had loaded the specimens at 28 days of age and kept the specimens immersed in water throughout the investigation. The explanation for the lower creep was that the water requirement of the slag concrete was lower than that of the control concrete thus resulting in lower paste content.

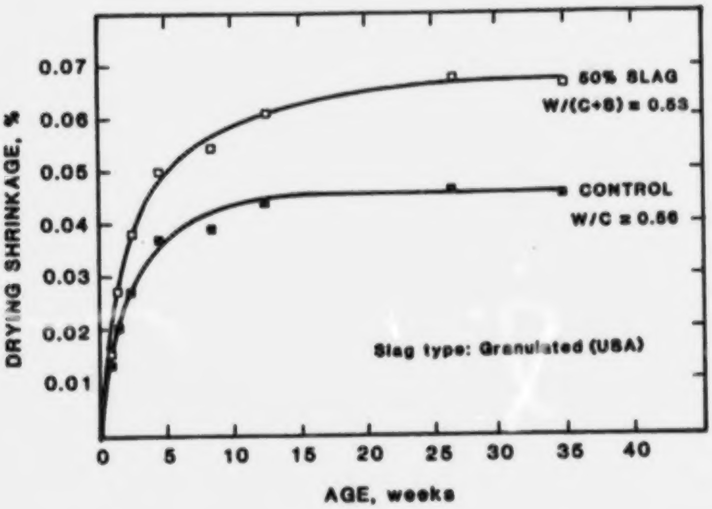

Fig. 3.18 — Drying shrinkage of air-entrained concrete: W/(C+S) = 0.53 (13)

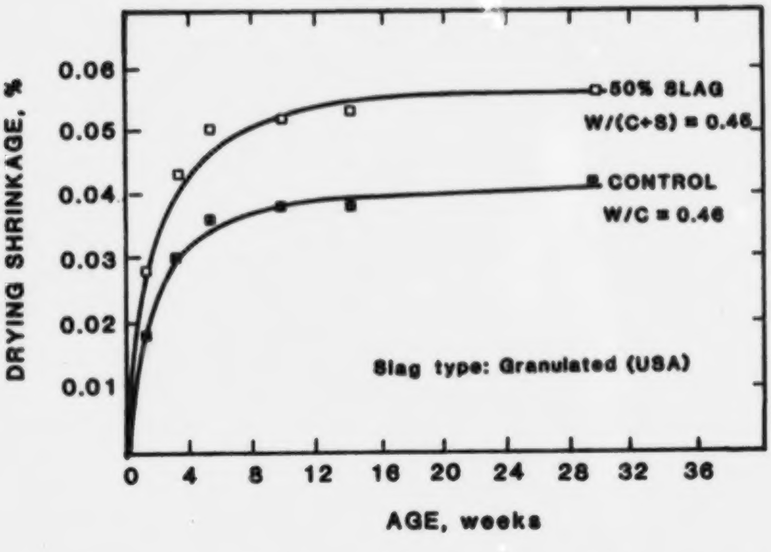

Fig. 3.19 — Drying shrinkage of air-entrained concrete: W/(C+S) = 0.45 (13)

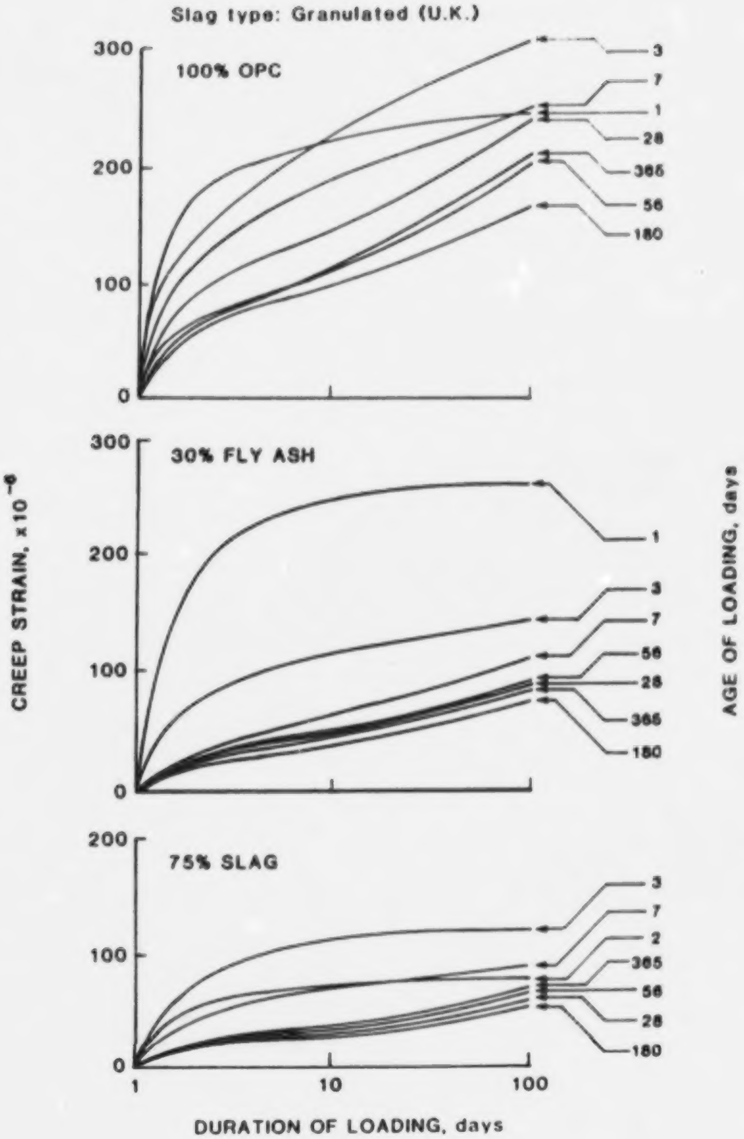

Fig. 3.20 — Creep of concrete with and without granulated slag loaded to constant stress-strength ratio of 25% (22)

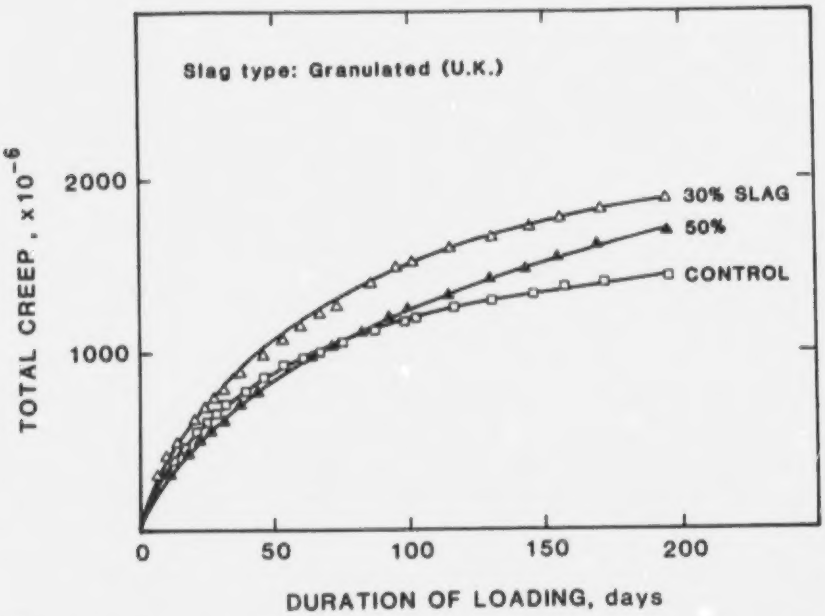

Fig. 3.21 — Effect of partial replacement of cement by granulated slag on total creep of concrete stored at 60% RH and 21°C: applied stress = 10 MPa (23)

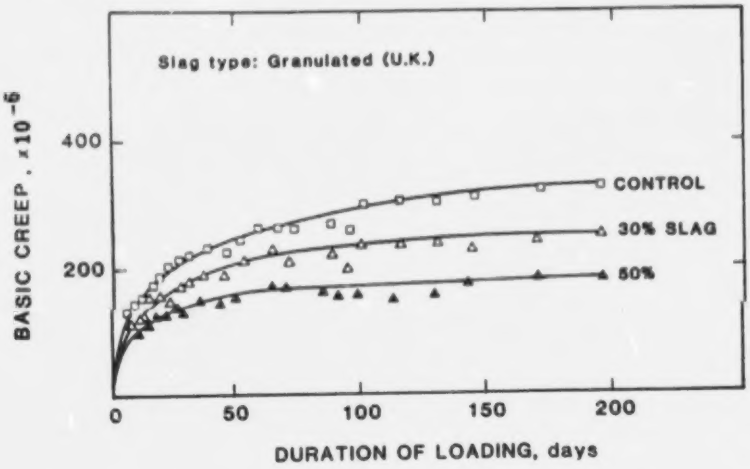

Fig. 3.22 — Effect of partial replacement of cement by granulated slag on basic creep of concrete stored in water at 22°C: applied stress = 10 MPa (23)

Permeability

The permeability of concrete depends mainly upon the permeability of the cement paste which, in turn, depends upon its pore-size distribution. Using mercury intrusion techniques, several investigators (24, 25) have shown that the incorporation of granulated slags in cement paste helps in the transformation of large pores in the paste into smaller pores, thus resulting in decreased permeability of the matrix and, hence, of the concrete. The exact mechanism by which the pore refinement occurs in hydrated slag–cement matrix is, however, not fully understood. Detailed data on the comparison of permeability of concrete with and without slags are not available, although it is an observed phenomenon that granulated slag concretes incorporating slags at up to 75% cement replacement have performed satisfactorily in exposure to sea water (26).

Temperature Rise

Bamforth (22) has reported investigations dealing with the in-situ measurements in mass concrete, in which part of the portland cement was replaced by granulated slag or fly ash. Three concretes were examined: a control mixture with portland cement content of 400 kg/m^3; a mixture having 75% of the portland cement replaced by a granulated slag from a source in the United Kingdom; and a mixture having 30% of the portland cement replaced by a fly ash. The high cement content was chosen to provide data for cement-rich structural concrete. The concrete was placed in 4.5-m deep foundations and the volume of concrete involved was 144, 147, and 212 m^3 for portland cement concrete, fly ash concrete, and slag concrete, respectively.

The temperature of the concrete at placing was recorded by thermocouples. The early-age temperature variation recorded at mid height for each foundation block is shown in Figure 3.23. The maximum temperature rise recorded at the centres of foundation blocks were:

- — portland cement concrete: 54.5°C rise, from placing temperature of 20.5°C
- — fly ash concrete: 47.5°C rise, from placing temperature of 21.5°C
- — granulated slag concrete: 46.0°C rise, from placing temperature of 18°C.

The effect of the cement replacement materials in each case was to reduce the peak temperature rise by about 8°C (15%). The temperature rises per unit weight of cementitious material were 13.6°C/100 kg for portland cement, 11.7°C/100 kg for portland cement–fly ash, and 11.6°C/kg for portland cement–slag combinations. Thus in mass concrete where low peak temperatures are essential to control thermal cracking, the use of slags may be advantageous.

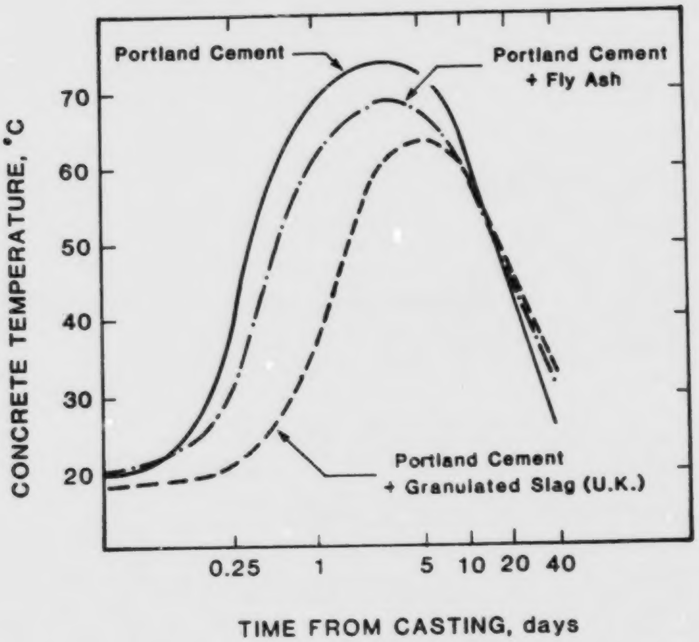

Fig. 3.23 — Peak temperatures for concrete made with fly ash and granulated slag (22)

Standards and Specifications

Several countries have published national standards and specifications to regulate the use of slags in concrete. These include Canada (27), the United States (28), and the United Kingdom (29), the latter being the most recent country to do so. The North American approach in the development of these specifications has been to develop performance-oriented documents which emphasize the strength-producing aspects of mortars incorporating slags. This approach is refreshing compared with the ASTM and Canadian specifications on fly ash. On the other hand, the recently published British standard BS 6699 has followed the more conventional and conservative approach; in addition to strength requirements on concrete incorporating slag, the standard sets limits on glass content, chemical modulus, fineness, and magnesia. This standard is far more restrictive than its North American counterparts (Tables 3.4 to 3.6).

In addition to a general specification to cover supplementary cementing materials, the Canadian Standards Association has published a standard dealing with cementitious hydraulic slag (30). This specification was developed primarily to cover the use of a pelletized slag produced in southern Ontario.

Table 3.4 — CSA Standard CAN3-A23 5-M82*: supplementary cementing materials and their use in concrete construction

Chemical Requirements

Property	Ground, granulated blast-furnace slag	Minimum frequency** of testing
SO_3, max., %	5.0	Lot or 1000 metric tons
Loss on Ingition, max., %	—	Lot or 100 metric tons

*From reference (27).

**When sufficient test data have been accumulated showing to the satisfaction of the owner that a source consistently complies with the requirements, the test frequencies may be reduced up to 10 times the stated value.

*Supplementary Optional Chemical Requirements**

Property	Ground, granulated blast-furnace slag	Minimum frequency** of testing
Moisture content, max., %	3.0	Lot or 100 metric tons

*From reference (27).

**When sufficient test data have been accumulated showing to the satisfaction of the owner that a source consistently complies with the requirements, the test frequencies may be reduced up to 10 times the stated value.

Physical Requirements

Property	Ground, granulated furnace slag	Minimum frequency* of testing
Slag Activity Index: with portland cement at 28 d, min. % of control	80	Lot or 1000 metric tons
Soundness: Autoclave expansion or contraction, max., %	0.5	Lot or 1000 metric tons
Fineness: when wet sieved on 45-µm sieve max. % retained	20	Lot or 100 metric tons
Uniformity Requirements: The relative density and fineness of individual samples shall not vary from the average established by the 10 preceding samples, or by all preceding samples if fewer than 10, by more than:		
Relative Density max. variation, from average, %	5	
Percentage retained on the 45-µm sieve, max. variation from average, percentage points†	5	

*When sufficient test data have been accumulated showing to the satisfaction of the owner that a source consistently complies with the requirements, the test frequencies may be reduced up to 10 times the stated value.

†If average is equal to 20%, then allowable variation = 15% to 25%.

Table 3.5 — ASTM Standard Specification C 989 for ground, iron blast-furnace slag for use in concrete and mortar*

Chemical requirements	
Sulfide Sulfur (S) max, %	2.5
Sulfate Ion Reported as SO_3, max, %	4.0

Alkali and strength limits of reference cement for slag activity tests		
Total Alkalies (Na_2O + 0.658 K_2O),	min%	0.60
	max%	0.90
Compressive Strength, psi, min, 28 days	5000(35 MPa)	

Physical requirements Item	
Fineness:	
amount retained when wet screened on No. 325 (45-μm) sieve, max %	20
Specific surface by air permeability, Method C 204 shall be determined and reported although no limits are required.	—
Air Content of Slag Mortar, max %	12

Slag Activity Index, min, %	Average of last Five Consecutive Samples	Any Individual Sample
7-Day Index		
Grade 80	—	—
Grade 100	75	70
Grade 120	95	90
28-Day Index		
Grade 80	75	70
Grade 100	95	90
Grade 120	115	110

* From reference (28).

Table 3.6 — British Standard BS 6699 for ground, granulated blast-furnace slag*

Requirement	Ground, granulated blast-furnace slag (ggbfs)
Minimum fineness (m^2/kg)	275
Minimum glass content	pure glass 40%: glassy particles 85%
Minimum concrete compressive strength: mean of 3 cubes (MPa)	
Age (days) 3	3 70% ggbfs combined
7	— with 30% OPC
28	22
Setting time	
initial (not less than)	45 min 70% ggbfs combined with 30% OPC
final (not greater than)	10 hr.
Soundness: maximum expansion	10 mm 70% ggbfs combined with 30% OPC
Maximum insoluble residue	1.5%
Maximum magnesia	14.0%
Sulphur:	2.0%
a) max present as sulphide	
b) max present as SO_3	n/a
Max loss on ignition:	3.0%
tropical climates	
temperate climates	4.0%
Chemical modulus:	
a) $\frac{CAO + MgO + Al_2O_3}{SiO_2}$, not less than	1.0%
b) CaO/SiO_2 not more than	1.4
Maximum moisture content	1.0%
Maximum heat of hydration, (J/kg):	
7 days	n/a
28 days	n/a

* From reference (29).
n/a = not applicable.

4. CONCLUSIONS

The data on the properties of fresh and hardened concrete incorporating slag as a separate ingredient at a concrete batch plant are sparse. This sparsity is because it is only recently that slags have been used in the above manner described in North America and the United Kingdom. Based upon the published data reviewed, the following conclusions may be drawn:

- The slags have considerable potential as a partial replacement for portland cement in concrete. The most promising cement replacement levels for ready-mixed concrete are between 25 and 50% of slag on a weight basis.
- The properties of fresh concrete are affected to some degree by the incorporation of slag; increased dosages of air-entraining admixtures are required to entrain a given amount of air, and the final setting time of concrete is delayed significantly.
- In general, the early-age compressive strengths of concretes incorporating slags are lower than that of the control concrete. This fact has to be taken into consideration in winter concreting operations.
- The flexural strength of slag concrete is comparable with, or greater than, the corresponding strength of the control concrete, which can be a decided advantage for concrete used in highway and airport pavements.
- The drying shrinkage of slag concrete has been reported to be higher than that of the control concrete. Additional investigations are needed to confirm this.
- The Young's modulus of elasticity of slag concrete is comparable with that of the normal portland cement concrete; data on creep are too limited to make any valid comparisons.
- Research is needed to develop more thorough and long-term data on mechanical and elastic properties, and durability of concretes incorporating slag as a separate material at a concrete batch plant.

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CHAPTER 6

BLAST-FURNACE SLAG CEMENT MORTAR AND CONCRETE: DURABILITY ASPECTS

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1. INTRODUCTION

The durability characteristics of materials used in the design of structures as well as their mechanical properties needs to be evaluated (1,2,3). Maintenance and replacement of structures from material failures increase the cost of construction. Nearly 40% of the total resources of the building industry in the USA is applied to the maintenance and repair of existing structures (3).

Generally, durability is defined as the capability of a material to maintain its good behavior and performance in conditions of safety under the foreseen circumstances of service and during the predicted service time.

Specifically, durability may be defined as the resistance of concrete to internal and external physical and chemical actions and to mechanical effects.

It is believed that increased durability of cement concretes incorporating blast-furnace slag results from a finer pore structure and reduced contents of easily leached calcium hydroxide in the hardened cement paste. Subsequently, the volume previously occupied by the calcium hydroxide is also filled in with hydration products, resulting in a less permeable material. Permeability controls the physical and chemical processes of degradation caused by the action of migrating water; therefore, permeability to water determines the rate of deterioration.

This chapter is one of a three-part series dealing with durability of mortar and concretes incorporating blast-furnace slag. The durability topics discussed include the resistance to sulphate attack, sea water, alkali–aggregate reaction, repeated cycles of freezing and thawing, and carbonation in mortar and concrete incorporating pelletized or granulated slags.

2. RESISTANCE TO SULPHATE ATTACK

Sulphates attack concrete and affect its coherence and strength. Resistance of concrete to sulphate attack is improved by partial replacement of portland cement with ground, granulated blast-furnace slag (1,2,3). In Germany (4), France (5), and the Netherlands (6) cements with a high content of blast-furnace slag have been used for many years and are considered appropriate for use in a high-sulphate environment.

Many explanations have been given with respect to the behavior of slag cements,* mainly attributing to the slag the ability to fix the Ca^{2+} that take part in the attack by sulphates. Hydrated portland cements with more than 5% potential C_3A** will contain most of the alumina in the form of $C_3A{\cdot}C\overline{S}{\cdot}H_{18}$ (monosulphate hydrate) (3). When the cement paste comes in contact with sulphate ions, the $Ca(OH)_2$ produced by hydration of the portland cement will react with the alumina-containing hydrates, producing ettringite:

$$C_3A{\cdot}C\overline{S}{\cdot}H_{18} + 2CH + 2\overline{S} + 12H \rightarrow C_3A{\cdot}3C\overline{S}{\cdot}H_{32}$$

The expansion resulting from the sulphate attack is related to the presence of ettringite. The mechanism by which ettringite causes expansion is a subject of controversy (3).

Expansion can also be caused by the formation of gypsum:

$$Na_2SO_4 + Ca(OH)_2 + 2H_2O \rightarrow CaSO_4{\cdot}2H_2O + 2NaOH.$$

In the case of attack by $MgSO_4$:

$$MgSO_4 + Ca(OH)_2 + 2H_2O \rightarrow CaSO_4{\cdot}2H_2O + Mg(OH)_2; \text{ and}$$
$$3MgSO_4 + 3CaO{\cdot}2SiO_2{\cdot}3H_2O + 8H_2O \rightarrow 3(CaSO_42H_2O) +$$
$$3Mg(OH)_2 + 2SiO_2{\cdot}H_2O.$$

Sodium sulphate attack produces NaOH which is responsible for the high alkalinity in the system, and which is essential for the stability of the calcium silicate hydrates (CSH). For the case of $MgSO_4$ attack the reaction produces poorly soluble and low-alkalinity $Mg(OH)_2$ which alters the stability of the CSH in the system and which causes, in turn, further attack of the CSH by the $MgSO_4$ solution (3).

An important factor affecting the reaction is the diffusion rate of the ions in the porous system (Table 2.1). Kondo et al. (7) measured the diffusion coefficient in hardened portland and in blended cements and concluded that, with age, the diffusion coefficient in a slag cement mortar diminishes faster than the diffusion coefficient in a portland cement mortar. Also, permeability to water is an important factor because water is necessary for the mechanism of the reactions causing expansion. Results of a study carried out by Bakker (2) show that a slag mortar is 10 to 100 times less permeable to water than a portland cement mortar, independently of the water-to-cement ratio (Figs. 2.1 and 2.2).

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*Hereafter, pelletized or granulated blast-furnace slag will be designated as slag.

**The abbreviations used by cement chemists are:
$C = CaO$; $S = SiO_2$; $A = Al_2O_3$; $\overline{S} = SO_3$; and $H = H_2O$.

Table 2.1 — Diffusion coefficients of various ions for portland cement (CP) and blast-furnace slag cement (CHF) (W/C = 0.5)*

Ion	Mortar age, days	$D_m(10^{-8}\ cm^2/s)$	
		CP	C.H.F.
Na^+	3	7.02	1.44
	14	2.38	0.10
K^+	3	11.38	2.10
	14	3.58	0.21
Cl^-	5	5.08	0.42
	103	2.96	0.04

*From reference 2.

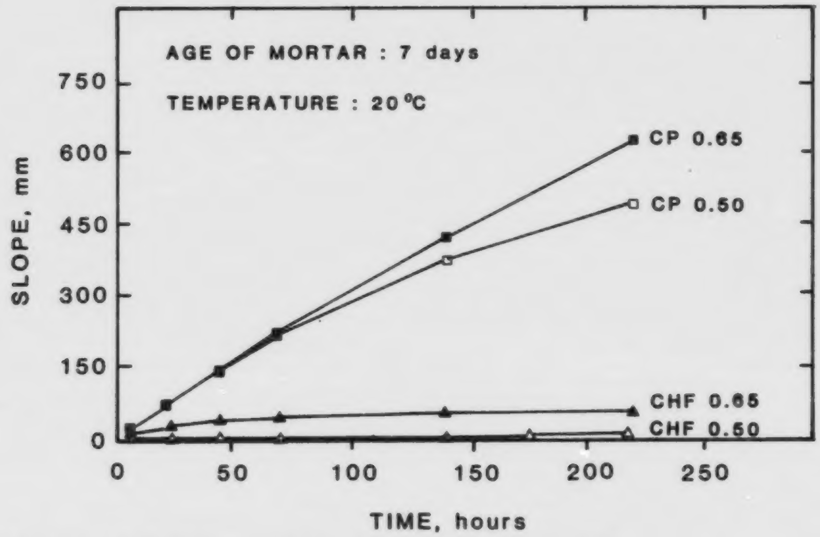


Fig. 2.1 — Relative permeability of mortars at seven days (2)

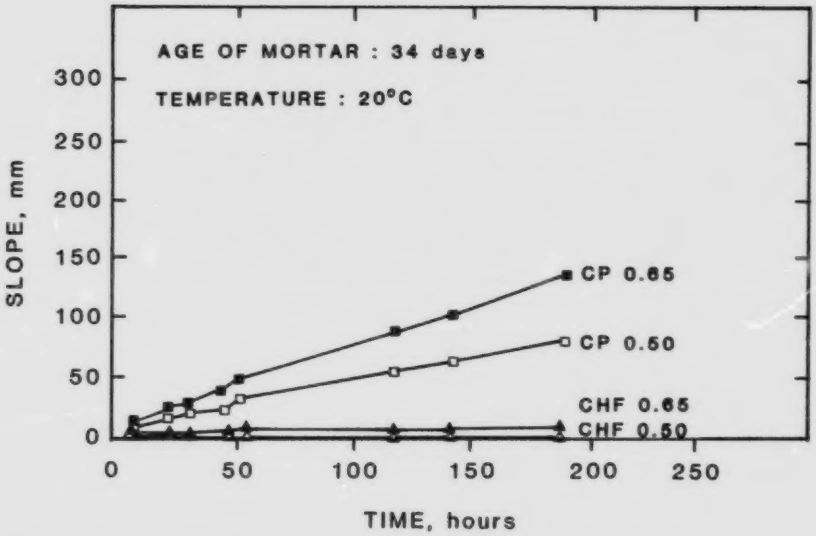


Fig. 2.2 — Relative permeability of mortars at 34 days (2)

In Canada, two independent studies (8,9) have shown that mixes of 50% pelletized slag and 50% CSA Type 10 (ASTM Type I) normal portland cement mortar and concrete are equivalent in sulphate resistance to CSA Type 50 (ASTM Type V) (sulphate-resistant) portland cement. The results of the studies provided the technical basis for using pelletized slag cement as a supplementary cementing material for sulphate resistance concrete in accordance with Canadian Standards Association CAN3-423-Current. Acceptance standards for such usage have been developed by the Ontario Ministries of Transportation and Communications and of the Environment. Based on the monitoring program for sulphate resistance that was in progress for six years, it was clear that specimens with blends of 50% pelletized slag and 50% Type 10 (normal) portland cement were performing in a way equivalent to CSA Type 50 (sulphate-resistant) portland cement for both concretes and mortars. The CSA Type 10 portland cement contained up to 12% C_3A, and the slag was reported to have 7% Al_2O_3 (9). The tests involved storage of the specimens in severe conditions (3000 ppm sulphate solution) and in accelerated conditions (50 000 ppm sulphate solution) (Fig. 2.3).

Hogan and Meusel (10) carried out a study that showed high resistance to sulphate attack when the granulated slag proportion exceeded 50% of the total cementitious material; ASTM Type II cements were used.

Results of recent studies carried out by Frearson (11) confirm the inferior resistance to sulphate attack of ordinary portland cements and of blends of both ordinary and sulphate-resisting portland cement containing lower levels

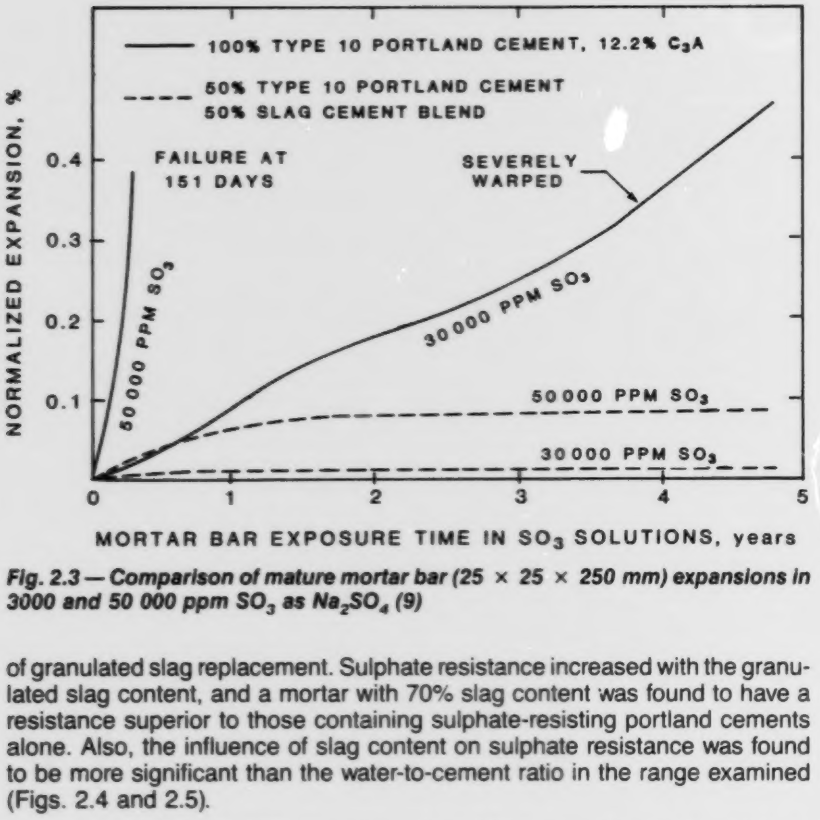


Fig. 2.3 — Comparison of mature mortar bar (25 × 25 × 250 mm) expansions in 3000 and 50 000 ppm SO_3 as Na_2SO_4 (9)

of granulated slag replacement. Sulphate resistance increased with the granulated slag content, and a mortar with 70% slag content was found to have a resistance superior to those containing sulphate-resisting portland cements alone. Also, the influence of slag content on sulphate resistance was found to be more significant than the water-to-cement ratio in the range examined (Figs. 2.4 and 2.5).

According to Ludwig (12), the cements exhibiting resistance to sulphate attack are:

- portland cement with a C_3A content ≤ 3 wt %;
- slag cement with $\geq 70\%$ slag content; and
- non-standard cements such as high-alumina and supersulphated cements.

Ludwig (12) stated that the high sulphate resistance of the special portland cements and slag cements in dense concretes results from the simultaneous penetration of sulphate ions and leaching of hydrated lime from the cementstone leading to reduction of the pH value and the portlandite content.

Bakker (13) found that slag concretes with a high slag content display an increased resistance to sulphates because of the low permeability of the concrete to different ions and water, as shown by the diffusion coefficient values (Table 2.2).

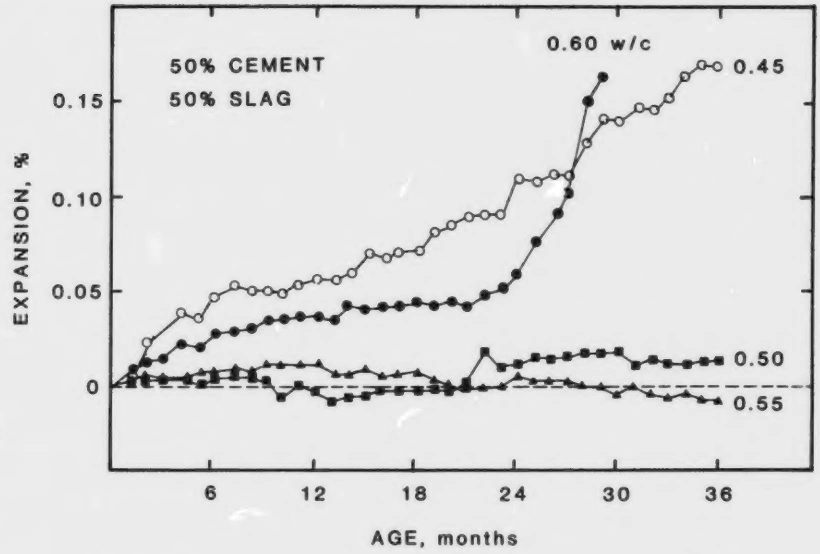


Fig. 2.4 — Expansion of 50% OPC/50% slag 'A' mortar prisms (11)

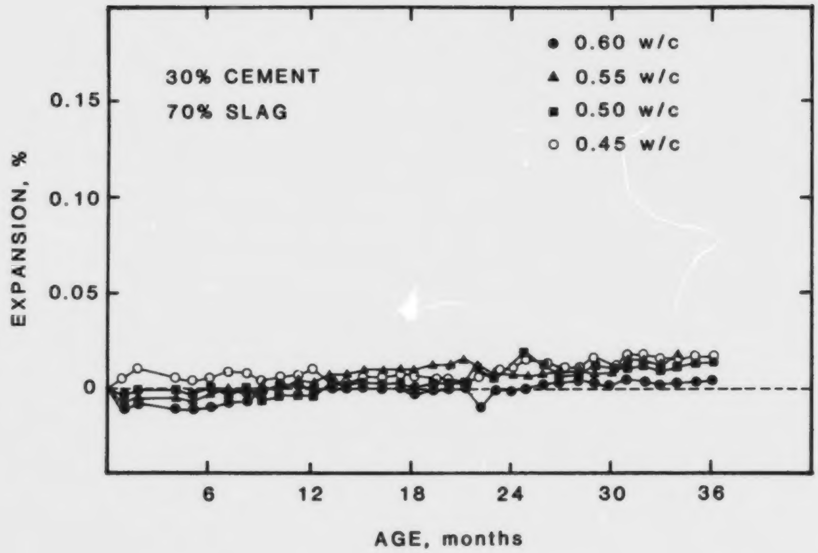


Fig. 2.5 — Expansion of 30% OPC/70% slag 'A' mortar prisms (11)

Table 2.2 — Diffusion coefficients of Na, K, and Cl ions in hardened cement paste and mortars made with portland and blast-furnace cement after different hardening times*

Diffused ion	Hardening time, days	W/C	$D_m(10^{-8}\ cm^2/s)$ OPC	BFC	Slag content
Na^+	3	0.50	7.02	1.44	75
	14	0.50	2.38	0.10	75
	28	0.55	1.47	0.05	60
	28	0.60	3.18	0.05	60
	28	0.65	4.73	0.06	60
K^+	3	0.50	11.38	2.10	75
	14	0.50	3.58	0.21	75
Cl^-	28	0.55	3.57	0.12	60
	28	0.60	6.21	0.23	60
	28	0.65	8.53	0.41	60
	5	0.50	5.08	0.42	75
	103	0.50	2.96	0.04	75
	60	0.50	4.47	0.41	65

*From reference 13.

Hogan and Meusel (10) reported a study carried out by Mather (14), using the lean mortar bar test designed by Wolochow (15). Mather stated that this procedure duplicates exposure to natural sulphates in which the cement or cement and slag hydrate to a considerable degree before the sulphate becomes available to the interior of the pastes. Figure 2.6 shows a marked improvement in resistance to sulphates, expressed as expansion, of the blended cement mortars over the control cement mortar. Results of the study carried out by Hogan and Meusel (10) on one cement and on three levels of cement replacement by slag indicate that, as the slag replacement of portland cement is increased, the resistance to sulphates improves (Figs. 2.7 and 2.8). According to the data developed with this test method, mixtures of Type II cement and granulated slag at 40 to 60% replacement will result in blends with superior resistance to sulphate attack.

Where granulated slag is used in sufficient quantities, several changes occur that improve resistance to sulphate attack. These changes include:

- The C_3A content of the mixture is proportionally reduced depending on the percentage of slag used. However, Lea (16) reported that increased sulphate resistance not only depends on the C_3A content of portland cement alone, but also on the Al_2O_3 content of the granulated slag. Lea further reported that sulphate resistance increased where the alumina content of the slag is less than 11%, regardless of the C_3A content of the portland cement when blends with 20–50% granulated slags were used.

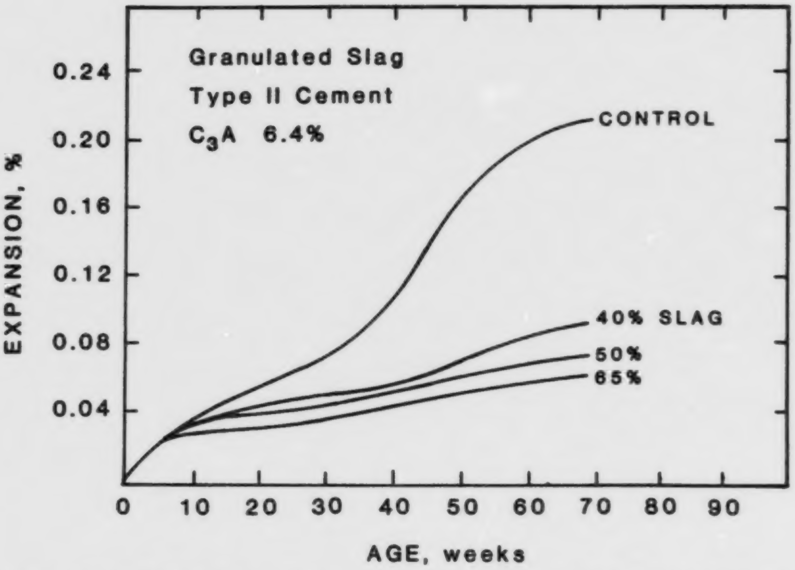


Fig. 2.6 — Sulphate resistance of mortar bars: Wolochow test method (Type II/I portland cement) (10)

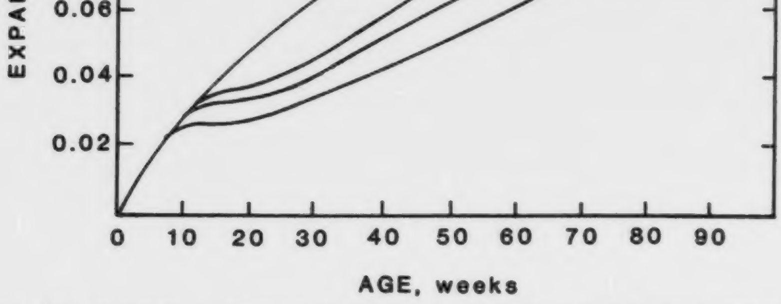


Fig. 2.7 — Sulphate resistance of mortar bars: Wolochow test methods (LTS 21 Type II) (10)

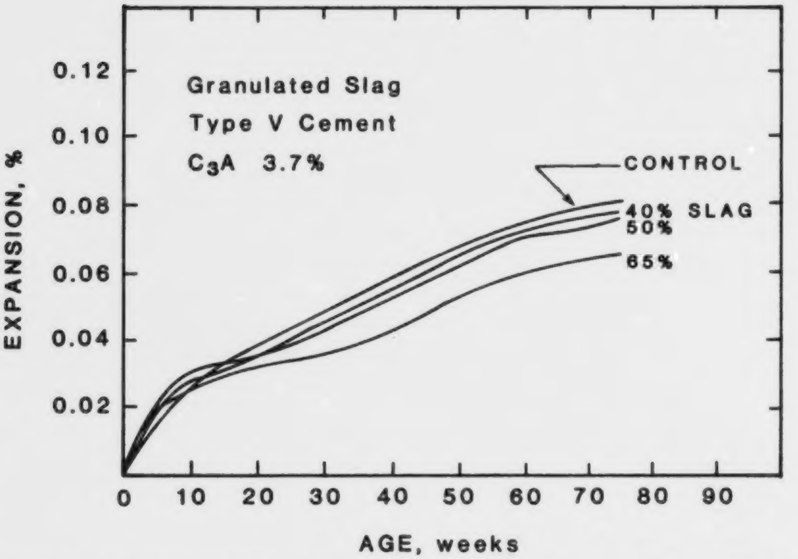


Fig. 2.8 — Sulphate resistance of mortar bars: Wolochow test method (LTS 51 Type V) (10)

- Through the reduction of soluble $Ca(OH)_2$ in the formation of calcium silicate hydrates (CSH), the environment for the formation of ettringite is reduced.
- Resistance to sulphate attack is greatly dependent on the permeability of the concrete or cement paste (13,17,18). The formation of CSH in pore spaces, usually occupied by alkalis and $Ca(OH)_2$, reduces the permeability of the paste and prevents the intrusion of aggressive sulphates.

Mehta (19) tested pastes incorporating natural pozzolans, rice husk ash, and granulated slag. The 28-day old paste of the blended cement containing 70% blast-furnace slag showed excellent resistance to sulphate attack. There were hardly any large pores present in the hydrated paste, although the total porosity (pores >45Å) was the highest among all the cement tested. The direct relationship between sulphate resistance of a cement and the slope of its pore-size distribution plot in the range 500–45Å, probably shows that the presence of a large number of fine pores is associated with improved sulphate resistance of the material (Fig. 2.9). Although the total porosity of the cement containing 30% slag was considerably less than the cement containing 70% slag, the former was not found to be sulphate resistant. On the basis of the test results, Mehta proposed that the chemical resistance of blended portland cements results mainly from the process of pore refinement which is associated with the pozzolanic reactions involving the removal of $Ca(OH)_2$.

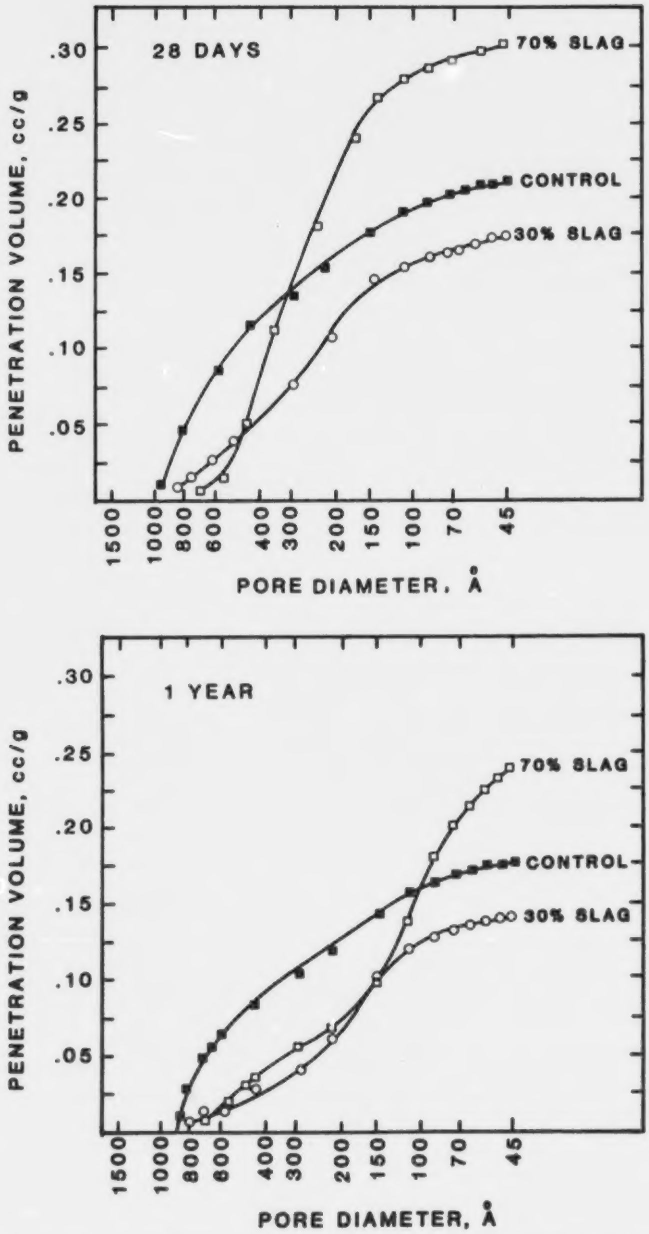


Fig. 2.9 — Pore-size distribution of hydrated cements containing 30 or 70% granulated blast-furnace slag (19)

3. RESISTANCE TO SEA WATER

Sea water contains sulphates and also attacks concrete. In addition to the chemical action, crystallization of the salts in the pores of the concrete may result in its disruption owing to the pressure exerted by crystal growth.

Crystallization takes place at the point of evaporation of water, so this form of attack takes place in concrete only above sea level. The salt solution rises in the concrete by capillary action, and hence, attack takes place only when water can penetrate into the concrete. Thus, permeability is a very important factor. Concrete subjected to alternating wetting and drying is attacked severely, whereas permanently immersed concrete is attacked least. The progress of attack by sea water is slowed when the pores in the concrete are blocked by the deposition of $Mg(OH)_2$.

In some cases the action of sea water on concrete is accompanied by frost, wave impact, and abrasion, all of which aggravate the damage.

The action of sulphate in sea water on concrete is rather similar to that of sulphate-bearing ground water, but the attack in the former case is not accompanied by expansion of the concrete. The absence of expansion is partly due to the presence in the sea water of a large quantity of chlorides which inhibit the expansion; gypsum and calcium sulphoaluminate are more soluble in a chloride solution than in water so they either do not form or are leached out by the sea water.

In the case of reinforced concrete, the absorbed salts establish anodic and cathodic areas: the resulting electrolytic action leads to an accumulation of the corrosion on the steel with a consequent rupture of the surrounding concrete. Therefore, the effects of the sea water are more severe on reinforced concrete than on plain concrete. A well-compacted concrete and good workmanship, especially in the construction of joints, are particularly important, as is the performance of the cement. Aluminous, sulphate-resisting, portland–blast-furnace slag and portland–pozzolan cements give good results (20).

Regourd et al. (21) studied mortar cubes that had been exposed to sea water since 1904 at the port of La Rochelle. They concluded that all portland slag cements with a slag content >60% perform well in sea water. In the case of lower slag content the $MgSO_4$ reacts with the $Ca(OH)_2$ from the C_3S and C_2S hydration and produces gypsum. The gypsum reacts with the aluminates to form expansive ettringite.

Mehta (3), on the other hand, supports the idea that the deterioration of concrete by sea water is not characterized by expansion, but rather is affected by erosion or loss of the solid constituents from the mass. Mehta proposes that ettringite expansion is suppressed in environments where $(OH)^-$ ions have been replaced by Cl^- ions.

In sea water, well-cured concretes containing large amounts of granulated slag or pozzolan usually outperform reference concretes containing only portland cement, partly because the former contains less uncombined $Ca(OH)_2$ after curing. In permeable concretes the normal amount of CO_2 present in sea water is sufficient to decompose the cementitious products. The presence of calcium silicocarbonate (thaumasite), calcium carboaluminate hydrate (hydrocalumite) and calcium carbonate (aragonite) have been reported in cement pastes derived from deteriorated concretes exposed to sea water for long periods.

Guyot et al. (22) reported that a portland cement with 15% of added slag behaved similarly to a portland cement meeting the French requirements for work in sea water (corresponding to an ASTM Type II cement). Cements with high contents of slag performed well, and good correlation was found between the residual strengths and slag content (Fig. 3.1) The influence of C_3A was not apparent in spite of the large number of cements examined and the high degree of variation in C_3A content (Fig. 3.2).

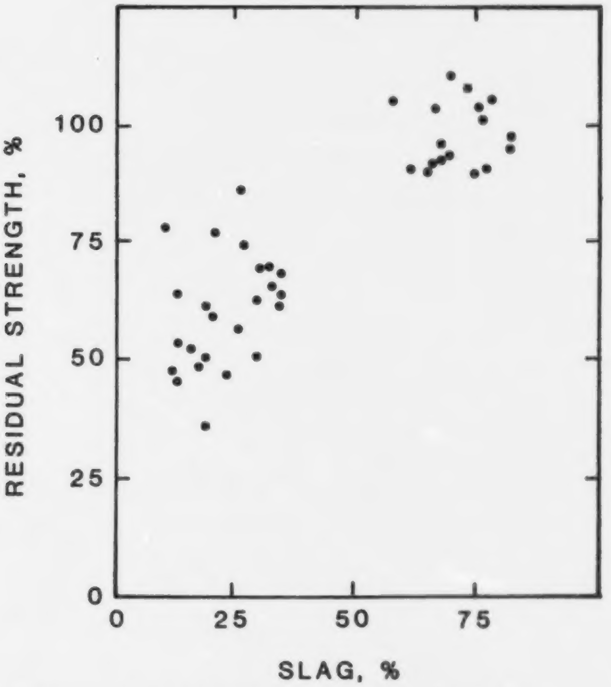


Fig. 3.1 — Influence of slag on parts immersed in sea water (22)

More recently, results were published (23) of a long-term study undertaken by the Canada Centre for Mineral and Energy Technology (CANMET), Energy, Mines and Resources Canada. The study deals with the durability in a marine environment of portland cement concrete incorporating slag, fly ash, silica fume, and superplasticizers. The marine environment chosen was Treat Island, Maine, an outdoor exposure station operated by the U.S. Corps of

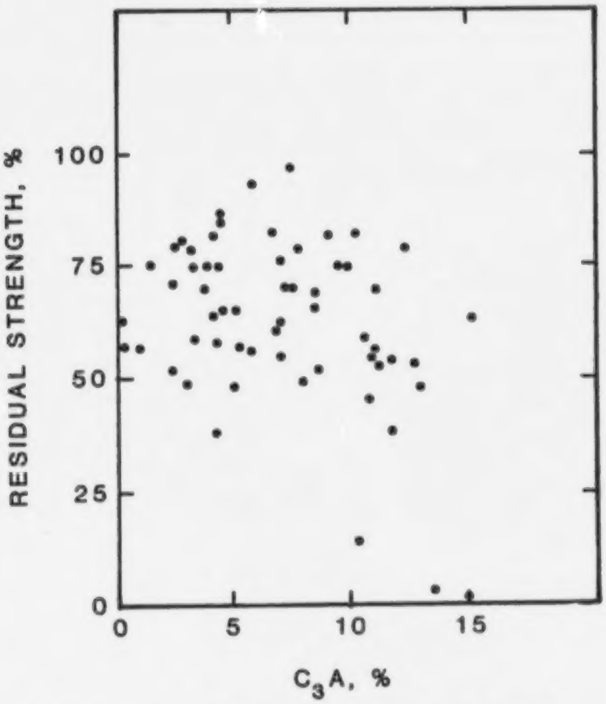


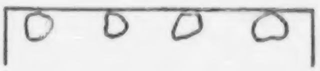
Fig. 3.2 — Influence of C_3A on parts immersed in sea water (22)

Engineers. Pelletized blast-furnace slag from a plant in Hamilton was used in investigations performed in 1978, 1979, and 1980. Granulated slag from a plant at Sparrows Point, New York, was used for studies in 1982. Visual ratings were classified as described in Figure 3.3.

Air-entrained concrete prisms exposed in 1978, at W/(C + S) of 0.60 and with 65% pelletized slag, have started to show severe deterioration after seven years of exposure and have visual ratings of 4. This deterioration implies that prisms with high percentages of the slag used at W/(C + S) of 0.60 even though air-entrained, may not have inherent strength for long-term durability under the exposure conditions encountered on Treat Island. There is increasing surface deterioration in all test prisms with increasing ratio of water-to-cementitious materials and increasing percentage replacement of cement with slag. Test prisms with a W/(C + BFS) of 0.40 and incorporating 65% slag show almost no surface deterioration and have a visual rating of 1. Concrete prisms incorporating 80% of the granulated slag as a replacement for cement are in satisfactory condition after three years of exposure, and have a visual rating of less than 1 regardless of the water-to-cementitious materials ratio. Because of the short exposure time, no direct comparison can be made between the pelletized and the granulated slag.

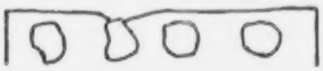
(i) RATING OF 0 :

Less than 15 aggregates are exposed



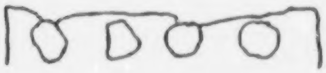
(ii) RATING OF 1 :

More than 15 aggregates are exposed



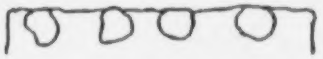
(iii) RATING OF 2 :

50% of the aggregates immediately below the surface are exposed



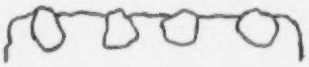
(iv) RATING OF 3 :

80% of the surface aggregates are exposed



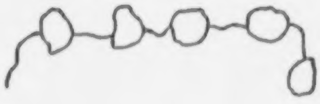
(v) RATING OF 4 :

Surface aggregates are exposed over 20% of their perimeter



(vi) RATING OF 5 :

90% of the surface aggregates are exposed over one half of their perimeter



(vii) RATING OF 6 :

95% of volume of specimen remaining

(viii) RATING OF 7 :

80% of volume of specimen remaining

(ix) RATING OF 8 :

50% of volume of specimen remaining

(x) RATING OF 9 :

20% of volume of specimen remaining

(xi) RATING OF 10 :

Specimen disintegrated

Fig. 3.3 — Visual rating system used to evaluate test prisms at Treat Island

4. REDUCTION OF EXPANSION DUE TO ALKALI–SILICA REACTION

In concrete containing reactive siliceous aggregates, slag cements are preferable to portland cements, which are rich in alkalis (24). Smolczyk (25) tested 30 different types of cement mixed with ground Pyrex glass and concluded that the expansion resulting from the alkali–silica reaction decreases with increasing granulated slag content. An addition of 70% slag to a portland cement can move the admitted limit of Na_2O from 0.6% to 2% without risk of degradation of the concrete. Calleja (26) stated that in the case of a possible expansion that can occur because of the use of susceptible siliceous aggregates, portland cements, whether low in alkalis or not, are not the best materials for making concrete that will be free of damage by expansion. Slag cements and pozzolanic cements seem to be more appropriate, partially because they allow a higher total alkali content in clinker, as established in most of the standards.

Some investigators (25) have explained the favorable behavior of slag cements by their fixation of the sodium ions in the alkali–aggregate reaction. Smolczyk (27) also found that the alkali ions are released to the pore solution. The effect of the blast-furnace slag is to lower the permeability of the concrete to the ions and to water.

$$SiO_2 + 2NaOH \xrightarrow{H_2O} Na_2SiO_3{\cdot}nH_2O$$

The Na^+ reacts with compounds almost insoluble in water, such as the SiO_2. The rate at which the ions move towards the insoluble components in a porous media is an important factor in the reaction. Kondo et al. (7) have determined the diffusion coefficients in portland cement and in granulated-slag cement mortars. They concluded that, after three months, the diffusion of the ions in the slag cement mortar is 75 times smaller than the diffusion in portland cement mortars. The results are confirmed by other investigators who calculated diffusion coefficients from diffusion measurements on hardened portland cement paste and mortar (see Table 2.2).

Research undertaken at the Concrete Research Institute of the Dutch Cement Industry and by other investigators (27) confirms that the reason for a high resistance to the alkali–silica reaction is the low permeability of these concretes to different ions and to water (28). The low permeability is due not only to the amount of gel formed but also to the locality where the gel is precipitated, i.e., the gel can block a pore when portland cement and slag grains are close to each other.

The potential alkali–aggregate reactivity for combinations of portland cement and granulated slag was investigated by Hogan and Meusel (10) using ASTM Test C 227; the aggregate used was Pyrex glass, known to be highly reactive (Fig. 4.1). The data indicate that the expansion of mortar bars made with slag–cement mixtures and Pyrex glass is significantly less than for those bars made with portland cement alone. The cement used for these tests had an alkali content of 0.51% sodium oxide equivalent, which conforms to the ASTM specification for portland cement C 150 requirement for low-alkali cement. These test results indicate that the replacement of high-alkali cement with slag reduces alkali–aggregate reactivity expansion.

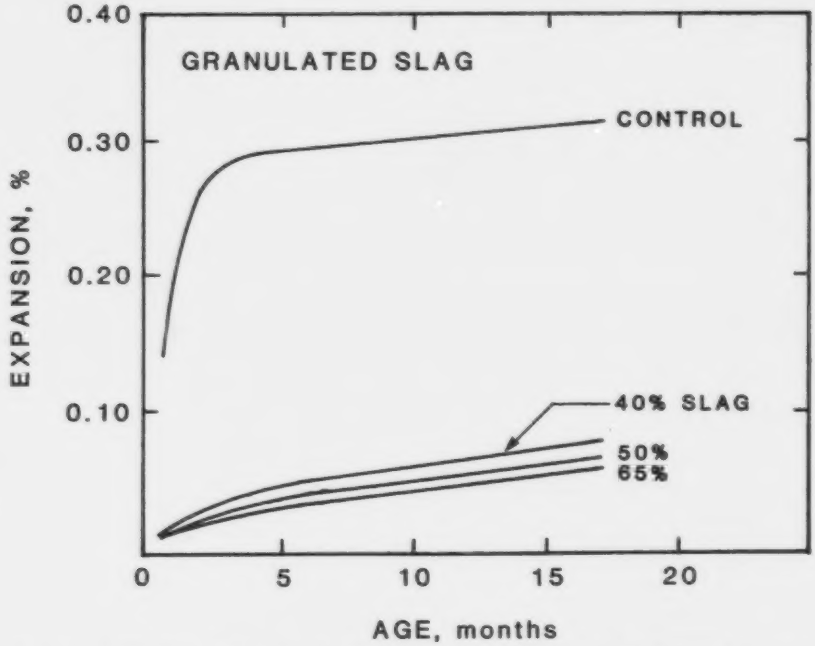


Fig. 4.1 — ASTM Test C 227 potential alkali–aggregate reactivity for various slag replacements (10)

Suppression of the alkali–aggregate reaction by the addition of slag was cited by Mather (14), who suggested that an alkali limit for portland slag cements, that have a performance equal to that of 0.60% Na_2O for portland cements alone, could be as high as 1.20% Na_2O equivalent.

Ludwig (12) carried out a study in which three different granulated slags replaced 35 wt % of cement, resulting in a reduction of 50% of the expansion. No correlation was found between this effect and the alkali content of the slags used. By replacing 65 wt % of portland cement by the slags no expansion was observed even after two years of humid storage. Mehta (29), however, showed that Type IS cements containing about 30% granulated slag, when investigated by the borosilicate-glass method [ASTM C 441-69(78)], were considerably different with regard to alkali–silica reactivity, thus proving that all portland–blast-furnace slag cements may not be safe for use with reactive silica aggregates.

Recently, Ludwig (12) investigated the effects of partial replacement of portland cement clinker with pozzolans, powdered zeolitic tuff, blast-furnace slag, and fly ash, on the minimization of the expansion phenomenon caused by alkali–aggregate reaction. Using the same portland clinker with a Na_2O equivalent content of 1.32%, a series of blended cements with different partial replacement of clinker and various additions were prepared. Their potential alkali reactivity was tested for up to two years, according to ASTM Standard C 441-81; the expansion was measured in bars prepared and mixed according to ASTM Standard C 227-81. Ludwig (12) demonstrated that all these products, in suitable ratios, neutralize the expansion phenomenon. Figure 4.2 (30) shows that the expansion of portland cement mortar is neutralized by replacement with pozzolanic additions ranging between 20 and 40%, whereas the

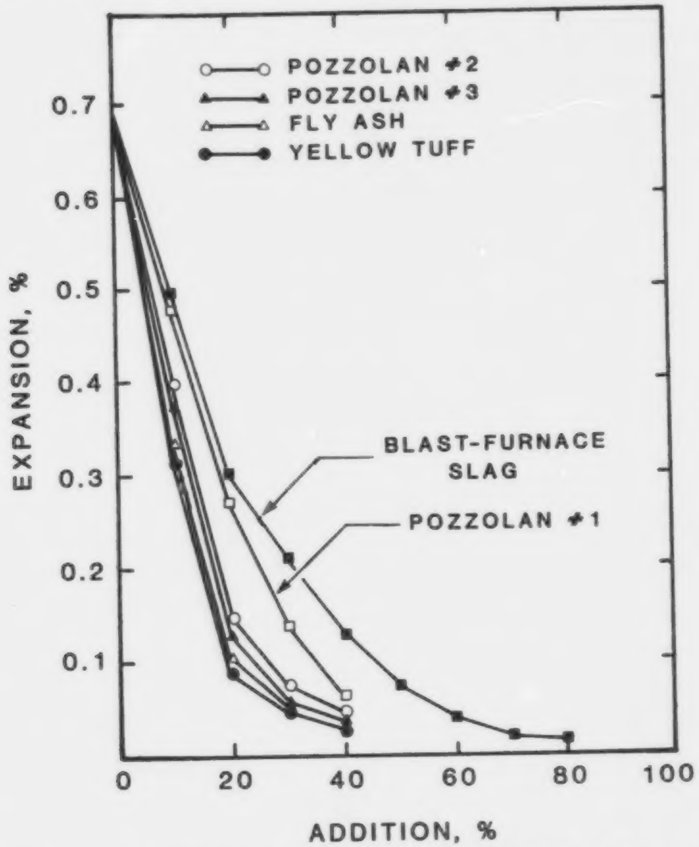


Fig. 4.2 — Effect of different partial replacements of the portland clinker with various additions, on the expansion of mortar, after two years, as a result of alkali–aggregate reactions (30)

same results are attained with blends containing 20–70% granulated slag. To neutralize alkali–aggregate expansion, therefore, selection of the type and the amount of addition must be strictly correlated with their influence on the strength properties of the resultant cement.

Yamamoto et al. (31) studied the reactions of alkalis and several types of slags using the chemical method (ASTM C 289) and the mortar bar method (ASTM C 227). They showed the beneficial effects of reducing expansion caused by alkali-reactivity by using granulated blast-furnace slag either as an aggregate or as a cementitious admixture in concrete. In the chemical test, granulated slag aggregate absorbed considerable amounts of NaOH solution whereas the chemical component of the residue was little changed, or remained in the innocuous area. They considered the mechanism of the action of granulated slag in reducing expansion and performed tests designed to determine whether the effectiveness of latent hydraulic materials is dependent on a similar action to that of pozzolans.

5. RESISTANCE TO REPEATED FREEZE–THAW CYCLES

Many studies are reported in which granulated blast-furnace slag has been used as partial replacement for portland cement in concrete submitted to repeated freeze–thaw cycles. Results of these studies indicate that when mortar or concrete made with granulated slag–portland cement were tested in comparison with Type I and Type II cement, their resistance to freezing and thawing in water (ASTM C 666, Procedure A) was essentially the same (32,33,34) provided the concrete was air-entrained.

More recently, Hogan and Meusel (10) tested freeze–thaw durability of specimens cast of air-entrained concrete with 50% slag replacing portland cement, and of a control containing only portland cement. The specimens were stored for 14 days in a moist-curing chamber and were subsequently placed in a freeze–thaw chamber. Tests were carried out under Procedure A, ASTM C 666 (Table 5.1). Although a measurable difference was found in the durability factors of the two concretes after 301 freeze–thaw cycles, both were rated as frost-resistant, disregarding the difference in weight loss and negligible expansion.

Malhotra (35) reported results of tests performed in an automatic unit capable of performing eight freeze–thaw cycles per day (ASTM C 666, Procedure B). The percentage of slag used as replacement for normal portland cement varied from 25 to 65 wt % of cement. Initial measurements were taken at 14 days. Subsequently, two specimens were placed in the freeze–thaw cabinet, leaving two companion specimens in the moist-curing room for reference

Table 5.1 — Resistance to repeated freeze–thaw cycles*

	Control	50% Slag and 50% cement
Lot	614	614
W/C	0.56	0.56
Air content, % (pressure)	5.5	6.0
Slump, mm**	82.6	82.6
Content, kg/m^3	149	149
Cement and slag content, kg/m^3	268	269
Weight, kg/m^3	2336	2326
Change in property freeze–thaw at 301 cycles**		
Expansion, %	+0.010	+0.026
Weight, %	−3.25	−2.42
Durability factor	98	89 relative durability factor = 91

*From reference 10.

**1 in = 25.4 mm, 1 lb/yd^3 = 0.59 kg/m^3, and 1 lb/ft^3 = 16 kg/m^3.

purposes. The specimens were examined visually after 50 freeze–thaw cycles. After about every 100 cycles the specimens were measured, weighed, and tested by resonant frequency and by the ultrasonic-pulse velocity method. The test was terminated at 700 freeze–thaw cycles. Durability of the exposed concrete prisms was determined from weight, length, resonant frequency, and pulse velocity of the test prisms before and after the freeze–thaw cycling, and relative durability factors (ASTM C 666) were calculated. The test results (Table 5.2) indicate that regardless of the W:(C + S) ratio and whether the concretes were air-entrained or air-entrained and superplasticized, these specimens performed excellently in freeze–thaw tests with relative durability factors greater than 91%. Some deviation from this behavior was justified by the fact that test prisms with slag addition were subjected to freeze–thaw cycling at equal ages rather than at equal compressive strengths with respect to the control specimens.

Virtanen (36) studied the effect of mineral admixtures on the properties of fresh and hardened concrete. The results of the study led to the following conclusions:

- in freeze–thaw tests, non-air-entrained concretes incorporating slag, fly ash, or silica fume showed poorer results than portland cement concrete; and
- air-entrained concrete made with slag, fly ash, or silica fume showed better frost-resistance than the corresponding portland cement concretes.

Table 5.2 — Summary of freeze–thaw test results for concrete Series B and D†

			Summary of freeze–thaw tests results									
			At zero cycles				At completion of 700 cycles					
Mix series	W/C + S*	Type of mix	Weight, kg	Length,** mm	Longitudinal resonant frequency, Hz	Pulse velocity, m/s	Weight, kg	Length, mm	Longitudinal resonant frequency, Hz	Pulse velocity, m/s	Durability factor, %	Relative durability factor, %
B	0.38	Control + AEA	8.703	2.89	5150	4717	8.693	2.90	5200	4747	102	100
		Control + AEA + SP	8.499	2.70	5150	4684	8.486	2.72	5138	4661	99	97
		25% slag + AEA	8.697	3.00	5300	4788	8.673	3.05	5225	4788	97	95
		25% slag + AEA + SP	8.540	2.96	5125	4684	8.517	3.01	5100	4656	99	97
		65% slag + AEA	8.622	2.74	5140	4684	8.626	2.91	4950	4568	93	91
		65% slag + AEA + SP	8.302	1.59	5025	4589	8.302	1.68	4875	4531	94	92
D	0.56	Control + AEA	8.331	2.56	5000	4568	8.299	2.56	5010	4600	100	—
		Control + AEA + SP	8.443	2.76	4980	4568	8.394	2.76	4980	4504	100	100
		25% slag + AEA	8.451	2.85	5000	4573	8.416	2.88	5000	4606	100	100
		25% slag + AEA + SP	8.544	2.83	5040	4639	8.483	2.91	5050	4622	100	100
		65% slag + AEA	8.465	2.61	4950	4546	***	2.88	****	****	—	59
		65% slag + AEA + SP	8.471	2.52	4930	4563	***	2.75	****	****	70	

†From reference 35.

* Water-to-cement + slag ratio.

**Gauge length of 345 mm should be added to this value to arrive at the exact length.

***Prisms failed at the end of 533 freeze–thaw cycles when the resonant frequency was 3840 Hz.

****Prisms failed at the end of 450 freeze–thaw cycles when the resonant frequency was 4150 Hz.

Results also showed that blast-furnace slag and silica-fume concretes have a higher resistance to freezing and thawing than do corresponding fly ash or portland cement concretes. Also, it was reported that the air content of concrete has the greatest influence on the resistance of concrete to freezing and thawing. When the strength and air content are kept constant, the addition of slag may slightly improve the resistance of concrete to freezing and thawing.

Pigeon and Regourd (37) studied the freeze–thaw resistance of cements with various contents of granulated blast-furnace slag. It was concluded that the observed good performance of the slag cements resulted from the dense and uniform structure of the hydrated pastes and the fine pore texture. The freeze–thaw resistance was estimated by the change of length, mass, and modulus of elasticity during curing and freeze–thaw cycling (Tables 5.3 to 5.5).

Nakamura et al. (38) showed that concrete with high resistance to chloride penetration and to freezing and thawing can be obtained by using classified slag fines.

Table 5.3 — Length changes of test specimens during curing and freeze–thaw cycling*

		Length change (10^{-6}m/m)**				
Mix	$\bar{L}$, μm	After 28 days curing	After 70 cycles	After 140 cycles	After 230 cycles	After 510 cycles
CPA 1	53	+119	−36	−83	−71	−48
CPA 2	103	+107	−36	−83	−36	−18
CPA 3	432	+107	−36	−83	−83	−48
CPA 4	443	+107	0	−60	−24	0
CPA 5	338	+107	−24	−60	−48	−48
CPA 6	367	+107	0	−36	−36	+24
CPJ 1	55	+119	−24	−60	−60	−36
CPJ 2	138	+83	0	−36	−36	−36
CPJ 3	529	+95	0	−60	−71	−83
CPJ 4	730	+107	+12	0	−24	−18
CPJ 5	679	+119	+36	+24	0	+48
CPJ 6	484	+95	+24	0	−12	+24
CHF 1	50	+119	+36	+12	0	+95
CHF 2	118	+83	+36	+36	+12	+54
CHF 3	780	+83	+12	−24	−36	+12
CHF 4	964	+48	0	−24	−36	+71
CHF 5	663	+60	0	0	+36	+333
CHF 6	696	+60	+12	0	+36	+226

*From reference 37.

**Each value is the average of the results obtained by the measurement of the three prisms (70 × 70 × 280 mm).

Table 5.4 — Changes in mass of test specimens during curing and freeze–thaw cycling*

Mix	$\bar{L}$, µm	Mass** on day 1, g	Mass change, g				
			After 28 days curing	After 70 cycles	After 140 cycles	After 230 cycles	After 510 cycles
CPA 1	53	2705	+50	−7	−7	−7	−4
CPA 2	103	2846	+46	−8	−8	−8	−7
CPA 3	432	3043	+49	−9	−9	−10	−14
CPA 4	443	3150	+49	−6	−6	−7	−5
CPA 5	338	3161	+42	−6	−6	−8	−13
CPA 6	367	3160	+43	−6	−7	−9	−11
CPJ 1	55	2722	+60	−15	−16	−19	−24
CPJ 2	138	2967	+51	−14	−14	−15	−19
CPJ 3	529	3192	+52	−9	−10	−11	−15
CPJ 4	730	3165	+45	−7	−8	−10	−19
CPJ 5	679	3162	+44	−5	−7	−12	−27
CPJ 6	484	3153	+45	−8	−10	−13	−24
CHF 1	50	2751	+60	−12	−13	−17	−27
CHF 2	118	2959	+42	−9	−12	−15	−19
CHF 3	780	3183	+37	−3	−3	−5	−6
CHF 4	964	3193	+31	−5	−7	−10	−15
CHF 5	663	3171	+30	−4	−6	−7	−15
CHF 6	696	3155	+31	−4	−6	−9	−15

*From reference 37.

**Each value is the average of the results obtained by the measurement of the three prisms (70 × 70 × 280 mm).

Table 5.5 — Changes in modulus-of-elasticity test specimens during curing and freeze–thaw cycling*

		Modulus of elasticity (MPa)**					
Mix	$\bar{L}$ (μm)	E on day 1	After 28 days curing	After 70 cycles	After 140 cycles	After 230 cycles	After 510 cycles
CPA 1	53	13314	23342	23349	23743	23780	24637
CPA 2	103	16817	28408	28147	28351	28923	30022
CPA 3	432	19893	34398	33956	34463	34909	36067
CPA 4	443	23676	37987	37177	37680	38223	39660
CPA 5	338	23176	37385	36625	37227	37282	38773
CPA 6	367	23650	38623	38140	38742	38712	40537
CPJ 1	55	14342	23127	23716	24104	24585	25280
CPJ 2	138	19102	30203	30590	31181	31634	32910
CPJ 3	529	22935	37734	38065	38567	39037	39867
CPJ 4	730	21642	37420	37534	37948	38679	40275
CPJ 5	679	20355	36508	36441	37172	37535	39663
CPJ 6	484	20937	36604	36659	37278	37907	39563
CHF 1	50	9856	23592	23868	24298	24661	26533
CHF 2	118	12448	29306	29105	30061	30346	32665
CHF 3	780	12557	36397	37226	37766	38304	40670
CHF 4	964	16668	36854	37251	38082	38533	40903
CHF 5	663	14313	34350	34754	35579	36104	38230
CHF 6	696	14128	34571	34903	35731	36175	38537

*From reference 37.

**Each value is the average of the results obtained by the measurement of the three prisms (70 × 70 × 280 mm).

6. CARBONATION

Concrete exposed to air will partially release its free water from the layers next to the surface. During the evaporation, the pore water in the concrete is replaced by air, and reactions between the CO_2 of the atmosphere and the alkali compounds of the concrete take place. This process between the CO_2 of the atmosphere and the hydration products of the hardened cement paste is called *carbonation*. The properties of the concrete, as well as the protective properties of the concrete against corrosion of reinforcing steel, are affected by these reactions.

Steel in the presence of high concentration of hydroxyl ions does not corrode. Bird (39) stated that this passivity is the result of the formation of a protective film of gamma ferric oxide on the surface of the steel. As long as this protective film is maintained by a high pH and is not disrupted by aggressive substances, complete protection of the steel against corrosion is assured. Carbonation can reduce the pH to an extent determined by the permeability of the concrete. Hamada (40) and Meyer (41) seem to agree that carbonation proceeds more rapidly in concretes incorporating slag than those made with ordinary portland cement. This finding has been disputed by Schröder and Smolczyk (42) who point out that comparative tests should be based on specimens of equal initial permeability rather than on specimens of equal age.

Meyer (41) stated that in a compacted concrete with dense aggregates and without air-entraining admixture the progress of carbonation depends largely upon the water-to-cement ratio (Fig. 6.1), the type of cement used (Figs. 6.2 and 6.3), and the storage conditions (Fig. 6.4). The depth of carbonation in concrete and mortar 2.5 years old having a water-to-cement ratio of 0.60 was taken as 100%. Depths of carbonation were related in per cent to that value.

Concrete made of blended cement showed higher depths of carbonation than those made of portland cement alone. In concrete incorporating slag, the depth of carbonation increased with an increasing percentage of slag. At a percentage of 50% blast-furnace slag the carbonation was 1.5 times as deep as in portland cement concrete, whereas it was twice as deep when the percentage of slag was 70%.

Concrete constantly stored in air will undergo the strongest carbonation. An approximately quadratic function exists between the depth of carbonation and the age of the concrete (see Fig. 6.4).

Kasai et al. (43) also showed that the carbonation depth of the blended cement is greater than that of the portland cement. The depth of carbonation could be estimated from the coefficient of air permeability (Fig. 6.5). Paillere et al. (44) obtained similar results demonstrating that the lowest amount of carbonation occurs in portland cement concrete and in concrete incorporating low amounts of slag. This finding is related to the high content of micropores formed at early ages in concrete made with cement containing slag. In concrete incorporating more than 18% slag, enhanced carbonation seemed to occur. Also, they showed that uncarbonated concrete resists freezing and thawing better than does carbonated concrete.

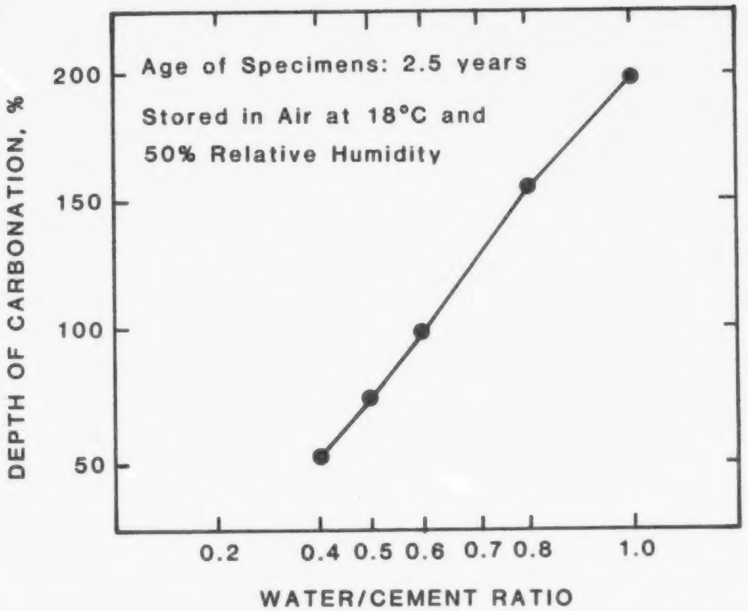


Fig. 6.1 — Effect of water-to-cement ratio on the process of carbonation (results of test series 3, 4, and 5) (41)

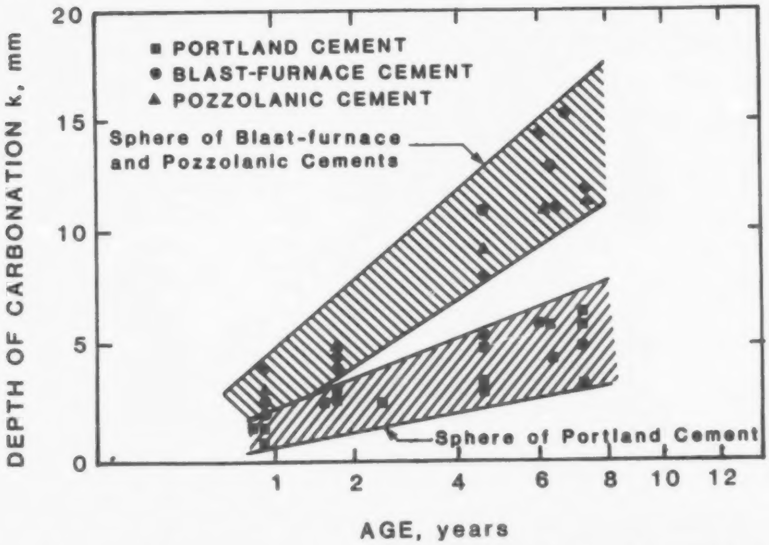


Fig. 6.2 — Effect of cement type on the progress of carbonation (results of test series 1) (41)

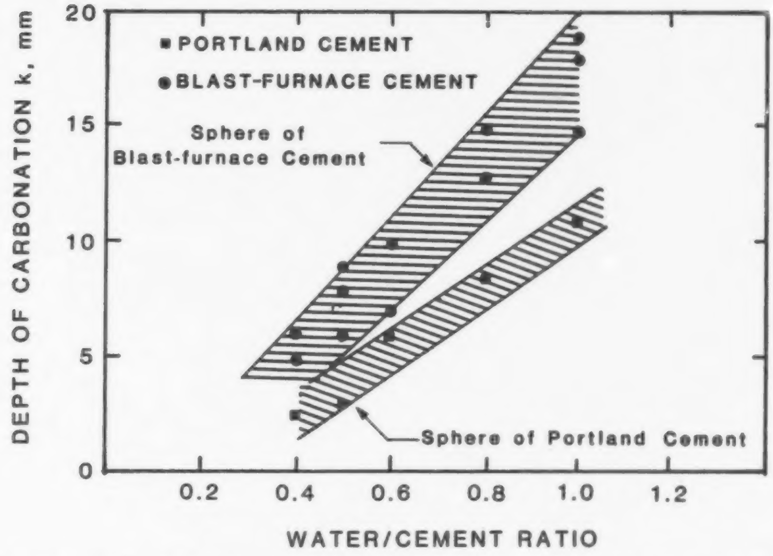


Fig. 6.3 — Effect of water-to-cement ratio and cement type on the depth of carbonation of concrete 2.5 years old (results of test series 3) (41)

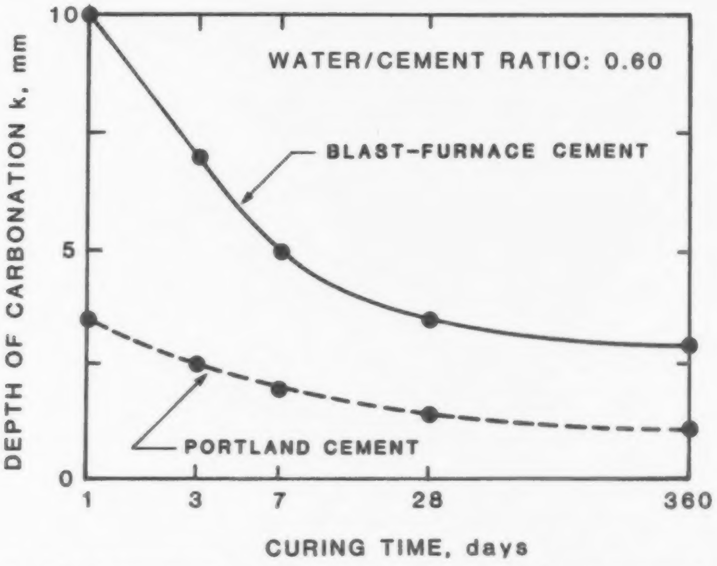


Fig. 6.4 — Effect of curing time on the depth of carbonation: Concrete stored after wet-curing for one year in open air but protected from rain (41)

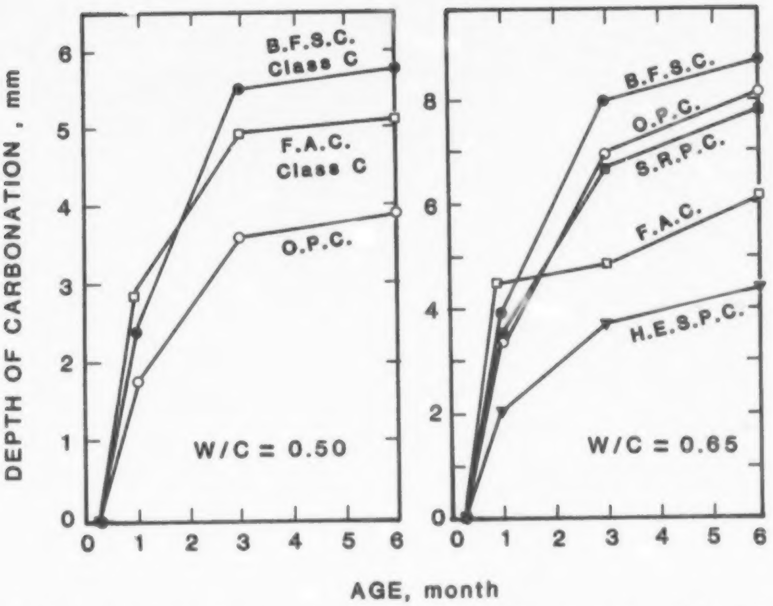


Fig. 6.5 — Relationship between age and depth of carbonation of mortar cured in water for seven days (W_7) (43)

With limited data, Litvan and Meyer (45) showed that the reason for the different rates of carbonation of portland cement concrete and portland cement concrete incorporating blast-furnace slag is suggested by the pore-size distribution analysis (Table 6.1). In Table 6.1 it is shown that carbonation of portland cement concrete caused a decrease in total porosity, from a nominal 15% to 11.5%, and a sharp reduction in pores with diameter less than 0.009 μm. At the same time the volume of large (>18 μm) and mid-size pores remained relatively constant. Carbonation rate decreased because of increased resistance to diffusion and longer path length. For concrete incorporating blast-furnace slag, the total porosity did not decrease and the volume fraction of the large and mid-size (0.35–0.019 μm) pores increased in both relative and absolute terms. Litvan and Meyer (45) concluded that the rate of carbonation in blended cement concrete exceeds that in portland cement concrete, and that carbonation increases the permeability of blast-furnace slag cement concrete because the small pores originally present become larger.

Table 6.1 — **Total porosity and fraction of pore volume in selected sizes of GBFSC and OPC concrete at various depths from exposed surface***

Depth, mm	Total porosity	Fraction of volume in pores, diam			
		>18 μm	0.35–0.019 μm	<0.009 μm	0.35–2 μm
			GBFSC		
3	12.0	0.8	6.5	0.6	2.0
3	11.3	0.6	6.3	0.3	2.0
3	13.7	0.5	7.4	0.3	3.0
3	13.5	0.6	7.3	0.3	2.8
Avg	12.65	0.62	5.9	0.37	
8	9.0	0.6	4.5	1.3	1.0
8	8.3	0.5	4.0	1.2	1.0
8	10.0	0.4	6.2	0.6	1.3
8	11.6	0.4	7.8	0.7	1.2
Avg	9.72	0.47	5.63	0.95	
24	12.5	0.4	6.1	3.0	1.2
38	12.4	0.4	1.8	6.5	1.1
46	10.7	0.4	1.4	6.4	0.9
70	11.9	0.3	1.7	6.5	1.0
			OPC		
3	11.2	0.3	4.8	1.4	2.1
3	12.1	0.4	4.8	1.6	2.3
3	11.5	0.4	5.2	1.4	1.5
3	11.4	0.4	5.1	1.7	2.5
Avg	11.55	0.37	4.98	1.52	
8	12.6	0.6	5.6	1.7	2.5
8	12.7	0.5	5.6	1.7	2.8
8	13.2	0.4	5.3	2.6	3.3
8	13.5	0.4	5.4	2.6	3.7
Avg	13.0	0.47	5.47	2.15	
24	14.9	0.5	5.1	3.5	4.7
40	14.3	0.3	5.0	3.0	4.7
40	14.1	0.3	5.2	2.7	4.5
Avg	14.2	0.3	5.1	2.85	
63	15.0	0.4	4.8	3.6	4.5

*From reference 45.

7. CONCLUSIONS

Through the limited data published in the literature on durability of mortar and concretes incorporating granulated or pelletized slag, it can be concluded that:

- Permeability controls the physical and chemical process of degradation, caused by the action of water movement, i.e., permeability to aggressive water determines the rate of deterioration.
- The increased chemical resistance of mortar and concrete incorporating more than 50% slag results mainly from the process of pore refinement which is associated with the pozzolanic reactions involving the removal of $Ca(OH)_2$.
- In spite of the encouraging results reported here, more research is needed on the durability of concrete incorporating granulated slag. Studies on resistance to aggressive water, alkali–aggregate reactivity, repeated cycles of freezing and thawing, and carbonation should be carried out to clarify some controversial aspects of durability of slag cement concretes.

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CHAPTER 7

A REVIEW OF THE PROPERTIES AND STRENGTH DEVELOPMENT OF NON-FERROUS SLAGS-PORTLAND CEMENT BINDERS

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1. INTRODUCTION

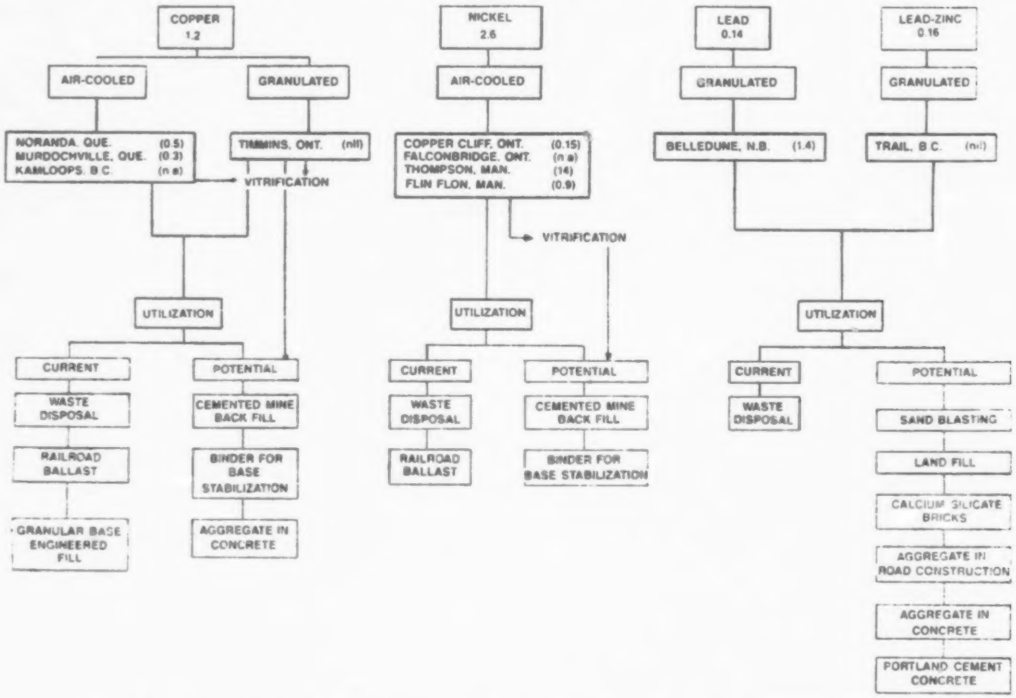
Wastes generated by the mining, mineral, and metallurgical processes contain metallic and mineral materials that are recoverable. Growing interest in such wastes has been caused by increasing exploration, mineral beneficiation, increasing cost of waste disposal, exhaustion of favourably located, high-grade mineral deposits, and legislation restricting mining operations near populated areas. These facts have prompted studies on the feasibility of recovering metals and minerals from more accessible mineral ore and from sources such as mineral wastes.

Basically, most of those mineral wastes not dumped in waste dumps are used as fillers, soil additives, aggregates, and railroad ballast. More important, however, are both the utilization of mineral wastes (such as slags) as portland cement replacement in cemented mine backfill and in concrete, and the realization that mineral wastes are by-products in which significant energy had been invested and lost through disposal (Fig. 1.1). Vitrification and grinding of ferrous wastes, such as blast-furnace slag, produce a material that can be added at the mixer as portland cement replacement in concrete manufacturing (1).

In Canada, vitreous (pelletized) iron blast-furnace slag is produced at a rate of 2.2×10^5 metric tons per annum in Hamilton, Ontario. In Sault Ste. Marie, Ontario, a plant is under construction to produce 200 000 metric tons per annum of granulated blast-furnace slag at the Algoma steel plant. About 45% of the blast-furnace slag produced in Hamilton is used in concrete manufacture (2).

Although the technology of utilization of granulated ferrous slags as cementing materials has been developed in Europe and North America, the utilization of non-ferrous slags as cementitious materials is not well established in concrete manufacture (3,4). The use of copper slags in mine backfill is current practice in Australia, where about 50% of the portland cement used in mine backfill at Mount Isa, Queensland, has been replaced by ground granulated copper slag, resulting in lower production costs (3).

In Europe, Australia, and Canada some copper, nickel, and lead slags have been evaluated for performance as cementitious components in mine backfill (4,5,6) and in concrete (7,8). Approximately 4.1×10^6 metric tons per annum of non-ferrous slags are produced in Canada, of which little is used as railroad ballast and engineering fill. The current accumulation amounts to about 17×10^6 metric tons.



CANADIAN NON-FERROUS SLAGS FOR RESOURCE AND ENERGY CONSERVATION

COPPER 1.2
AIR-COOLED
GRANULATED
NORANDA, QUE. (0.5)
MURDOCHVILLE, QUE. (0.3)
KAMLOOPS, B.C. (n.a)
TIMMINS, ONT. (nil)
VITRIFICATION
UTILIZATION
CURRENT
WASTE DISPOSAL
RAILROAD BALLAST
GRANULAR BASE ENGINEERED FILL
POTENTIAL
CEMENTED MINE BACK FILL
BINDER FOR BASE STABILIZATION
AGGREGATE IN CONCRETE
NICKEL 2.6
AIR-COOLED
COPPER CLIFF, ONT. (0.15)
FALCONBRIDGE, ONT. (n.a)
THOMPSON, MAN. (14)
FLIN FLON, MAN. (0.9)
VITRIFICATION
UTILIZATION
CURRENT
WASTE DISPOSAL
RAILROAD BALLAST
POTENTIAL
CEMENTED MINE BACK FILL
BINDER FOR BASE STABILIZATION
LEAD 0.14
GRANULATED
BELLEDUNE, N.B. (1.4)
LEAD-ZINC 0.16
GRANULATED
TRAIL, B.C. (nil)
UTILIZATION
CURRENT
WASTE DISPOSAL
POTENTIAL
SAND BLASTING
LAND FILL
CALCIUM SILICATE BRICKS
AGGREGATE IN ROAD CONSTRUCTION
AGGREGATE IN CONCRETE
PORTLAND CEMENT CONCRETE

Fig. 1.1—Production, location, and utilization of non-ferrous slags from Canadian sources (2)

Ferrous slags are siliceous or alumino-siliceous by-products of metallurgical processes. These slags possess little or no cementitious value, but in finely divided form and in the presence of moisture they react with alkali and alkaline earth hydroxides* at ordinary temperatures to form compounds possessing cementitious properties (9). Under the same conditions, cementitious properties can be conferred on non-ferrous slags.

Copper and nickel slags are extracted from sulphide concentrates by pyrometallurgical treatment. The process includes three different operations:

- **roasting**, in which sulphur is eliminated as SO_2 and iron is oxidized;
- **smelting**, in which the product of roasting is melted with a siliceous flux, forming a liquid iron-silicate slag which floats on the heavier, molten sulphide matte;
- **converting**, in which sulphur is driven off the sulphide melt and the remaining iron is oxidized and fluxed for removal as a silicate slag.

Converter slag is usually returned to the smelter because it is rich in metal content, whereas smelter slag is either discarded without further treatment or is granulated with excess water. These slags possess a high degree of hardness and porosity and vary in unit weight and in chemical composition because of differences in ore type, furnace or smelter operations, and slag-cooling procedures.

This study is a state-of-the-art review of the advances in research and in practical applications of copper, nickel, and lead slags. It is expected that a critical review could direct future research toward the use of significant amounts of a valuable resource.

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*This refers to NaOH, KOH, and $Ca(OH)_2$.

2. NATURE OF NON-FERROUS SLAGS

Chemical Composition

Despite the differences in process types, the slags are of similar chemical composition and all may be considered to be represented in the CaO–SiO_2–Fe_2O_3 system (Figs. 2.1 and 2.2).

The bulk composition of some Canadian slags is shown in Table 2.1 (10). A recent study on the characterization of Canadian non-ferrous slags (Table 2.2) shows that determination of the bulk chemical composition with an electron microprobe, operated at 15 kV accelerating voltage, differs somewhat from the chemical composition determined by analytical methods (11).

Glass Content

Data have been published by McGuire (12) on the glass content of non-ferrous slags from Canadian sources such as a nickel–copper electric-furnace slag granulated by quick quenching. The glass content was measured by X-ray diffraction and was reported to be 95% (13). The slag was too opaque for a reliable glass count by the optical method using polarizing light, similar to that adopted for quality control of iron blast-furnace slag (14).

Measurements of glass content by a method that uses scanning electron microscopy (SEM) and image analysis were reported by Douglas et al. (15) in a study on the hydration and the pozzolanic activity of ambient-cooled, and of quenched, copper reverberatory furnace* slags from Northern Quebec (Table 2.3). The glass content in the *air-cooled* slag was 45%; in the *quenched* slag, it was 75 to 95%. The composition of the glass was also reported (Table 2.4), showing the difference between the glass in the air-cooled slag and the quenched slag due to segregation of Al_2O_3, SiO_2, K_2O, and CaO during quenching. The results did not agree with those published by Roper et al. (16) who estimated a ratio of amorphous-to-crystalline phase of about 1:1 in a quenched copper reverberatory slag.

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*A reverberatory furnace is a furnace in which smelting of the concentrate takes place.

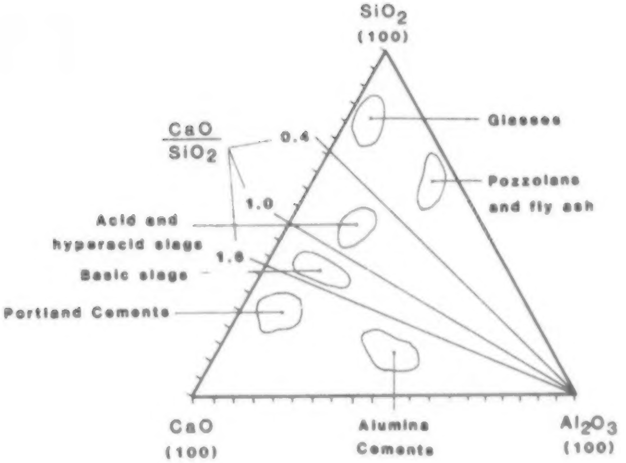
SiO2
(100)
CaO/SiO2
0.4
1.0
1.6
Glasses
Pozzolans and fly ash
Acid and hyperacid slags
Basic slags
Portland Cements
CaO
(100)
Alumina Cements
Al2O3
(100)

Fig. 2.1 — Representation of some cementitious materials in the system $CaO–SiO_2–Al_2O_3$

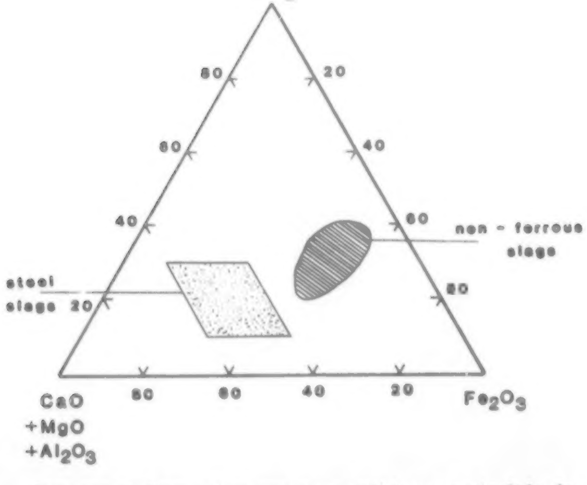
SiO2
80
20
60
40
40
60
non - ferrous slags
steel slags
20
80
CaO
+MgO
+Al2O3
80
60
40
20
Fe2O3

Fig. 2.2 — Representation of some cementitious materials in the system $CaO–SiO_2–Fe_2O_3$

Table 2.1 — Chemical analysis of Canadian non-ferrous slags (wt %) (10)

	A Lead (N.B) granulated	B Nickel (Ont.) air-cooled	C Nickel (Ont.) quenched	D Copper (Ont.) granulated	E Copper (Ont.) quenched	F Copper (Que.) air-cooled	G Copper (Que.) air-cooled	H Copper (Que.) quenched	I Copper (Que.) granulated
SiO_2	19.1	35.66	37.25	26.54	22.10	36.26	34.51	36.78	34.41
Al_2O_3	1.66	5.59	6.17	3.74	2.94	2.16	6.55	7.16	6.82
Fe_2O_3*	45.35	52.99	53.07	60.07	44.36	49.00	49.50	50.00	49.64
CaO	16.60	2.74	2.97	2.09	20.32	7.30	2.20	1.93	1.66
MgO	0.68	2.53	2.43	1.63	1.52	1.91	1.48	1.49	1.91
Na_2O	0.26	0.87	0.86	0.39	0.23	0.28	1.02	1.06	1.34
K_2O	0.25	0.65	0.62	0.33	0.98	1.26	1.01	0.96	0.66
TiO_2	0.14	0.32	0.33	0.14	0.12	0.13	0.35	0.39	0.28
MnO	0.09	0.07	0.07	0.10	0.08	0.08	0.10	0.09	0.08
Cu	—	—	—	1.10	—	0.48	0.43	0.41	0.48
Ni	—	0.23	0.25	—	—	—	—	—	—
Pb	4.84	—	—	—	—	—	—	—	—
LOI**	−5.75	−5.32	−6.00	−5.84	−4.39	−3.91	−5.24	−6.13	−4.73
S	1.30	1.46	1.39	1.28	0.45	1.01	1.20	1.13	1.00

---

*Total iron expressed as Fe_2O_3.

**LOI at 700°C. Negative values indicate a gain after ignition caused by oxidation of FeO and S^2.

Table 2.2 — Bulk composition of Canadian non-ferrous slags (wt %)

Element	J	I	C,D	G,H
FeO	55.1	44.6	50.3	40.9
CaO	2.1	16.7	3.5	17.6
ZnO	6.2	3.9	—	12.3
MgO	1.8	1.8	2.5	—
Al_2O_3	4.2	4.2	5.9	1.5
K_2O	0.4	0.4	0.7	0.2
CuO	—	—	—	0.1
PbO	—	—	—	3.0
TiO_2	—	—	0.3	—
SiO_2	32.1	30.6	36.6	23.5
S	0.8	0.6	1.5	1.6
Totals	101.9	102.8	101.3	100.7

S as sulphur only, not as SO_3 in oxide wt % column.

Table 2.3 — Copper slag* constituents determined by image analysis (15)

Sample	Fields	R**	Glass	Fayalite	Spinel	Sulphide
G,GB, Air-cooled	30	1.5	41±4	57±6	5±1	0.2
H,HA, Quenched	20	0.3–0.1	75–95	15–5	10–trace	—

*From Quebec.
**Ratio of crystals to glass.

Table 2.4 — Compositions of glass determined by electron microprobe in copper slags (Quebec)

	A Air-cooled slag	B Quenched slag
MgO	—	1.4 ± 0.03
Al_2O_3	14.5 ± 0.2	10.1 ± 0.2
SiO_2	45.8 ± 0.8	38.6 ± 0.5
K_2O	2.1 ± 0.2	0.6 ± 0.03
CaO	3.6 ± 0.7	1.7 ± 0.04
MnO	0.1 ± 0.02	0.1 ± 0.03
Fe_2O_3*	28.7 ± 3.8	39.4 ± 0.6
ZnO	5.3 ± 0.7	5.0 ± 0.2
PbO	0.8 ± 0.1	0.4 ± 0.1
Total	100.9	101.4

*Total Fe calculated as Fe_2O_3.

3. PROPERTIES OF NON-FERROUS SLAGS

Grindability

Information on grindability, energy requirements for grinding, and particle size distribution of ground non-ferrous slags is limited. Laneuville (5) reported the estimated power required to grind air-cooled and granulated nickel slags to various finenesses based on the duration of the grinds (Table 3.1).

Table 3.1 — Estimated kWh/t required to grind nickel slag (Ontario), calculated from grinding times (15)

	Air-cooled #1	Air-cooled #2	Granulated
Fineness (cm^2/g, Blaine method)			
3000	50	58	88
3500	65	65	107
3800	77	77	117
4000	83	83	128

The particle size distribution of a nickel–copper electric furnace slag, ground to a specific surface of 3 000 cm^2/g, was reported by McGuire (12) and is shown in Table 3.2. Size distribution of ground nickel slags from Copper Cliff, Ontario, tested for pozzolanic activity is shown in Table 3.3 (17).

More recently, a study by Douglas et al. (10) on the grindability of a number of Canadian copper, nickel, and lead slags compared it with that of a portland cement clinker containing 3% gypsum. For calibration of grinding time and energy consumption, the grinding energy requirement for portland cement clinker with 3% gypsum was taken as 31 kWh/t to develop a specific surface of 3 000 cm^2/g and 43 kWh/t to develop a specific surface of 4 000 cm^2/g. From this information about grinding energy consumption, a scale-up from laboratory mill to typical production mill was estimated as 1 min = 0.4 kWh/t, which is a value dependent on the specific laboratory.

Grinding data are given in Table 3.4, in terms of initial gradation, actual fineness (Blaine method), time to achieve specific fineness, and energy consumption for producing materials of 2 000, 3 000, 4 000, and 5 000 cm^2/g as well as specific gravity and per cent passing 45 μm (10).

Figure 3.1 shows the estimated energy consumption required for production grinding of the slag samples compared to that required to grind blast-furnace slag and portland-cement clinker with addition of gypsum to a specific surface of 4 000 cm^2/g. Grinding energy in increasing order, a comparison to an initial minus 75-μm size, major oxide composition, and estimated degree of vitrification are given in Table 3.5 (10).

From the data collected, it would appear that the grindability of non-ferrous slags is a function of the degree of vitrification. Slags with higher glass contents generally require more grinding time.

Table 3.2 — Particle-size distribution of granulated nickel slag (Ontario) ground to 3000 cm²/g (12)

Particle size (μm)	Weight percentage	
	Slag	Fill
+ 208	0.5	9.5
+1147	0.5	17.2
+ 104	0.7	16.7
+ 74	2.4	16.3
+ 53	9.7	11.3
+ 38	10.7	15.9
+ 27	29.7	12.2
+ 19	9.7	0.4
+ 13	9.9	0.2
+ 9	6.9	0.1
+ 7	4.42	0.06
+ 5	4.97	0.05
+ 3	4.97	0.05
+ 2	3.38	0.03
− 2	1.36	0.01

Table 3.3 — Size distribution, surface area, and specific gravity of ground nickel slags (Ontario) tested for pozzolanic activity (17)

(a) Size distribution (μm)	CC dump slag**	
	Wt %	Cum wt
+74	0.09	0.09
45	0.14	0.23
37	0.09	0.32
23	2.57	2.89
17	12.88	15.77
13	14.08	29.85
−13	70.15	100.00

(b) Surface area	S.A. (cm²)
Blaine (cm²/g)	4437
B.E.T. (m²/g)	20.9
(Gas adsorption)	
Specific gravity	3.30

**CC dump slag stands for Copper Cliff dump slag.

Table 3.4 — Energy consumption for grinding non-ferrous slags (10)

Sample	Average fineness measured, cm²/g				Grinding time, min				Energy consumed, kWh/t				Specific gravity*, cm²/g	% passing 45 µm			
	a	b	c	d	a	b	c	d	a	b	c	d		a	b	c	d
A	2029	2970	3891	5012	75	180	653	1335	30	72	261	534	4.00	76.52	85.55	87.59	88.52
B	2080	3044	4047	5026	50	75	115	178	20	30	46	71	3.54	70.57	83.68	91.49	94.59
C	2025	3098	3935	5019	60	75	120	210	24	30	48	84	3.45	69.49	86.94	91.32	95.16
D	2012	2976	4014	—	95	195	600	—	38	78	240	—	3.90	69.04	79.48	80.92	—
E	1995	3168	4095	4923	55	140	210	365	22	56	84	146	3.68	59.65	—	91.36	95.31
F	2034	3104	3955	4966	50	120	190	285	20	48	76	114	3.73	56.63	82.80	87.50	92.49
G	1979	3107	3927	4999	50	118	190	325	20	47	76	130	3.53	59.84	77.36	82.61	88.63
H	1985	3150	4138	4936	63	122	240	360	25	49	96	144	3.39	62.34	90.41	92.23	92.61
I	1987	2999	4049	5087	70	103	190	280	28	41	76	112	3.50	68.04	85.42	91.68	93.09
J	2032	2981	4118	4983	55	105	240	360	22	42	96	144	3.40	49.39	89.97	93.88	94.92
K	1975	2975	3968	—	70	240	600	—	28	96	150	—	3.58	63.12	71.77	73.82	—
L	1951	3031	3985	5038	65	140	240	420	26	156	96	168	3.40	66.04	92.42	93.79	94.47

Note: a, b, c, d indicate slags ground to 2 000, 3 000, 4 000, and 5 000 cm²/g, respectively.
*Specific gravity determined in samples ground to 4 000 cm²/g.

Table 3.5 — Grinding energy requirements and compositional characteristics of non-ferrous slags* (10)

Slag**	kWh/t	−75 μm %	SiO_2 %	Fe_2O_3 %	Vitrification***
B	46	8	35.7	53.0	crystalline
C	48	1	37.2	53.1	glassy/crystalline
F	76	2	36.3	49.0	crystalline
G	76	3	34.5	49.5	crystalline
I	76	1	34.4	49.6	glassy/crystalline
E	84	0.9	22.1	44.4	glassy/crystalline
H	96	0.5	36.8	50.0	very glassy
J	96	4	42.8	45.8	glassy
L	150	0.3	27.2	28.5	very glassy
(3000 Blaine 96) D	240	0.2	26.5	60.1	very glassy
(3000 Blaine 78) A	261	2	19.9	45.4	very glassy

Note: Energy requirement for grinding portland cement clinker is 44 MJ/t; for blast-furnace slag, 48 kWh/t to 4 000 Blaine.

* Slag K was not evaluated.

** Slags ground to 4 000 Blaine, cm^2/g, unless indicated.

***Qualitatively estimated by X-ray diffraction.

Pozzolanic Activity

Pozzolanic materials contain fine, active silica which reacts with lime and water to form stable cementitious, hydrated calcium silicates. For hydraulic cement mine backfill, fly ash, ground quenched-copper reverberatory-furnace slag, and ground blast-furnace slag are materials with proven pozzolanic activity (16). According to Thomas (18), three aspects have to be considered in the use of pozzolanic materials for hydraulic cemented mine backfill:

- reaction causing removal of lime, a material with potentially adverse effects;
- production of a stronger cement due to removal of lime, allowing strength development at a lower portland cement content;
- formation of additional cementing materials from the pozzolanic reaction, resulting in equivalent strength at lower portland cement content.

Experimental evidence of this approach was found by Thomas (3) in the results of a study on the pozzolanic properties of a granulated copper reverberatory-furnace slag which showed no obvious alteration after many years in a surface dump. The particle size analysis revealed essentially one component, approximately 2.54 mm in diameter. Test specimens were prepared from pulped mixtures of fill, portland cement, and the slag ground to a specific surface of 3 000 cm²/g. Strength increases with increasing slag additions at fixed cement content are shown in Figure 3.2. These results, concerning cost reductions in cemented fill production with no strength loss, were considered significant.

The same slag was tested at a later date in cemented mine fill at high slag/cement ratio (6). The fill contained 80 to 99 wt % of Isa Mine copper sulphide tailings, 1 to 5 wt % portland cement and 0 to 16 wt % slag (Fig. 3.3). Thomas (6) concluded that slag additions, indicated as non-beneficial at 1 wt % portland cement, were consistently beneficial at 3 and more wt % portland cement, and transitional in benefit at 2 wt % portland cement.

Pozzolanic activity tests on a granulated copper slag were carried out by various methods in Spain (4). The results of tests performed in accordance with ASTM C 618-73 method showed strength above 75 wt % of the control specimens.

Laneuville (5) determined the pozzolanic activity of air-cooled and of granulated nickel slags by ASTM C 595 method and reported that compressive strengths higher than the minimum 800 psi set out in the specifications were obtained with these slags ground to a specific surface in the range 3 800 to 4 000 cm²/g.

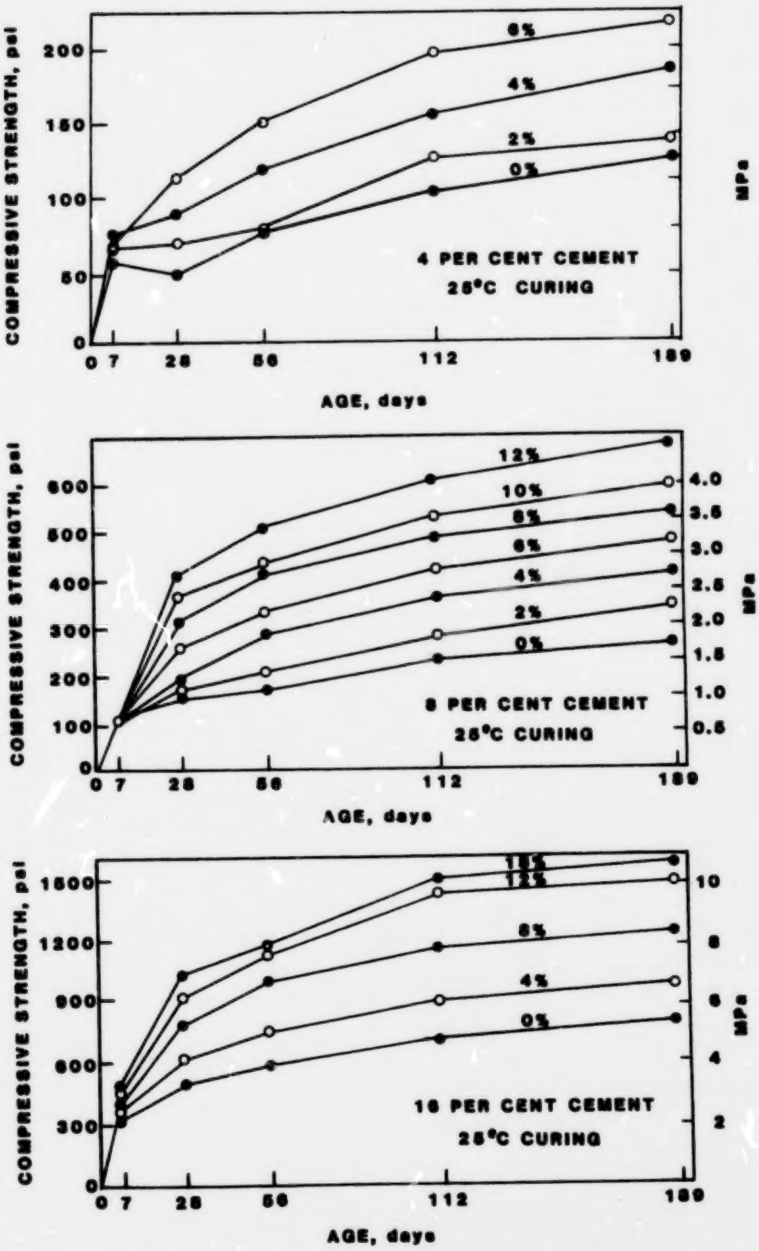

Fig. 3.2 — Curing curves demonstrating strengthening effect of ground copper reverberatory-furnace slag acting as a pozzolan with different cement contents (3)

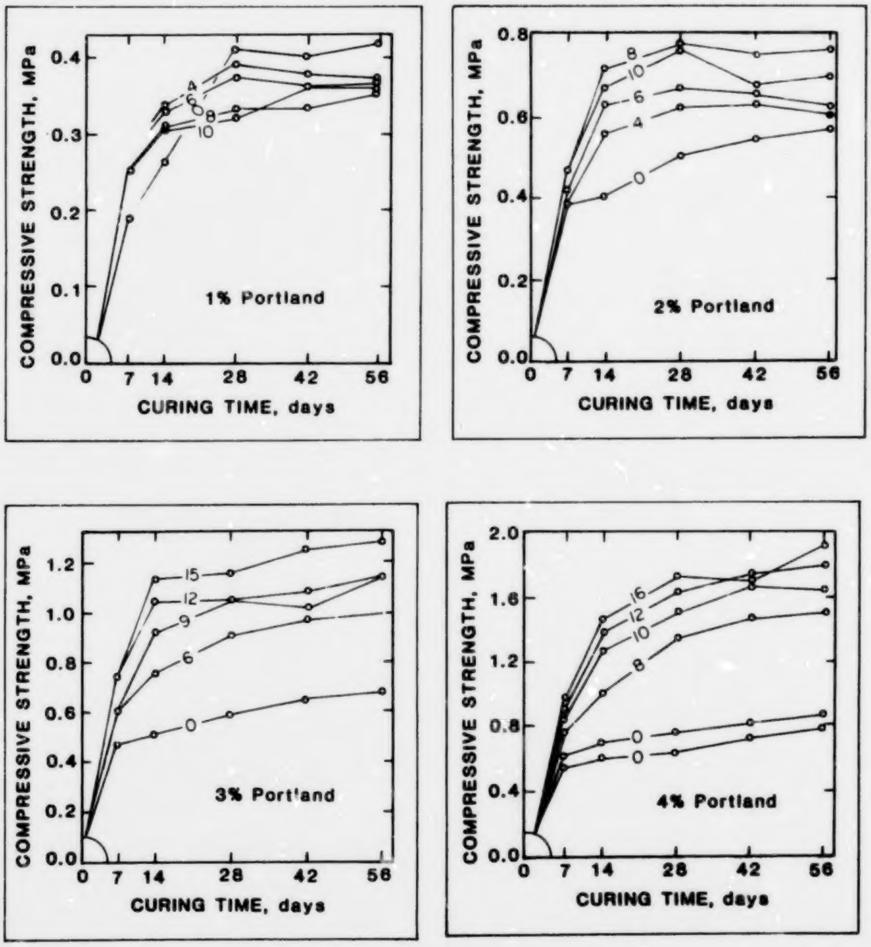

Fig. 3.3—Curing curves at 1, 2, 3, and 4 wt % portland cement and various copper reverberatory-furnace slag additions, as indicated on individual curves (6)

In Canada, strength gains with increasing contents of a granulated nickel–copper electric-furnace slag were measured by McGuire (12) in mixes containing 6 wt % of portland cement and a tailing fill of 2.96 relative density (Fig. 3.4). The strength gains were attributed to chemical bonding, derived from the hydration of a pozzolanic slag.

More recently, slag activity and pozzolanic indexes were determined in accordance with ASTM C 109* for the preparation of the test specimens, and with ASTM C 595** and C 989*** (10) for curing and testing.

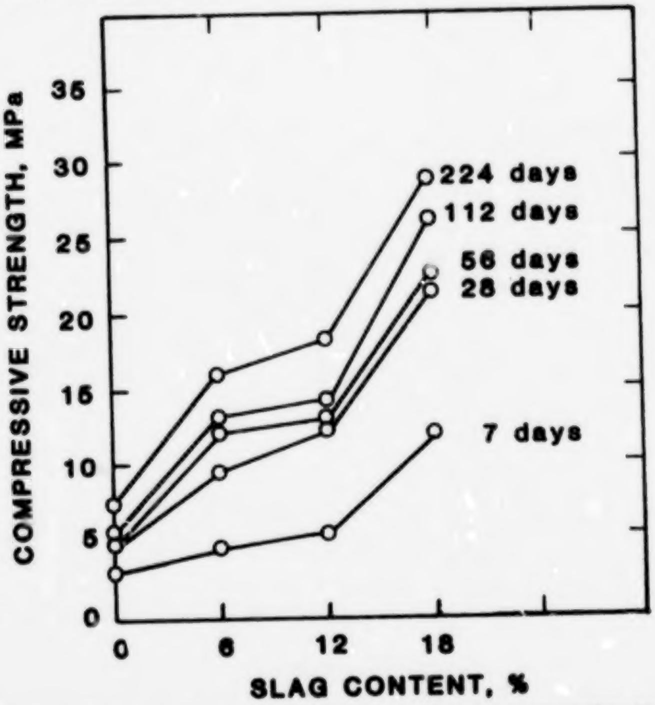

Fig. 3.4 — Effect of ground granulated slag on uniaxial compressive strength of consolidated fill containing 6% portland cement (12)

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*ASTM C 109: compressive strength of hydraulic cement mortars using 50-mm cube specimens.

**ASTM C 595: determination of pozzolanic activity and of slag activity index with portland cement on specimens cured in a moist room at 23°C for 24 h, and at 38°C in sealed containers after removing from the mold, for the balance of the time, to 28 days.

***ASTM C 989: determination of slag activity with portland cement. The following specifications were introduced: (a) replacement of 50% of the portland cement by the slag was done by absolute volume and not by weight, and (b) the specimens were cured at 23°C in the moist room to the specified age.

Tests were conducted at age 7 and 28 days according to a modified ASTM C 989 standard, where 50% of portland cement measured by absolute volume, was replaced by the ground non-ferrous slag, thus taking into account the different specific gravity of the slags (Table 3.6).

Significant strength development due to pozzolanic activity is shown in Figure 3.5. The strength development for 28 days curing at 38°C, for mortars with 20, 35, 50, and 70% ground non-ferrous slag replacing portland cement, is shown in Figures 3.6 to 3.8. Activators, such as NaOH, and the replacement of portland cement by cement kiln dust did not improve compressive strengths (10).

Effect of glass content on pozzolanic activity

The effect of glass content on the pozzolanic properties of Canadian non-ferrous slags can be assessed by comparing strength development data of air-cooled and of water-quenched slags (5,19).

Pozzolanic activity tests of binders for mine backfill were performed in Canada (20) with air-cooled and with quenched nickel and copper–nickel slags at different cement replacement levels. The chemical composition of the slags tested and the mixture proportions of the cemented backfill from which the test specimens were cast are listed in Tables 3.7 and 3.8.

Glass content of the air-cooled nickel reverberatory-furnace slag was estimated at less than 20%. The change in compressive strength was calculated on the basis of a standard incorporating 4.8 wt % of portland cement (Fig. 3.9). Maximum changes in strengths were observed after 14 days of curing for a sample incorporating 60% of air-cooled nickel slag. For unknown reasons, better performance occurred in long-term curing of test specimens of a mix incorporating an air-cooled, rather than water-quenched, copper–nickel slag. The mix contained 4.8% cement, 1.2% slag, and 94% tailings.

Results from recent studies on pozzolanic activity of Canadian air-cooled and of quenched non-ferrous slags (10,15) led to the conclusion that, (contrary to results of studies on blast-furnace slag), for non-ferrous slags the glass content and pozzolanic activity are not directly related. Test specimens of mortars with 35 and 70% cement replacement were prepared according to ASTM C 595, but cured at room temperature (15). Results of pozzolanic activity studies (Table 3.9) indicate that air-cooled copper slags could, depending on their fineness, outperform—or at least equal—the performance of quenched copper slags. Similar results were reported on pozzolanic tests carried out on granulated nickel, copper, and lead slags, according to ASTM C 595 (21). Pozzolanic and slag activity indexes are shown in Table 3.10.

Table 3.6 — Slag activity index of non-ferrous slags cured in moist room at 23°C for 50% portland-cement replacement by absolute volume (10)

	Slag																					
Blaine fineness	A		B		C		D		E		F		G		H		I		J		K	
	7d	28d	7d	28d	7d	28d	7d	28d	7d	28d	7d	28d	7d	28d	7d	28d	7d	28d	7d	28d	7d	28d
2000	35	52	28	39	34	48	29	52	29	46	28	33	30	39	30	44	24	38	25	38	38	55
3000	40	64	28	42	35	52	33	70	35	59	35	43	30	49	40	67	27	39	28	39	46	70
4000	45	81	32	48	37	59	34	73	40	67	38	52	35	56	47	83	33	59	39	59	54	91
5000	58	78	36	68	42	71	NG	NG	51	83	41	58	36	66	55	96	37	70	42	70	NG	NG

Notes: 1. Portland cement meets the requirements of ASTM C 989, "Specification for ground blast-furnace slag for use in concrete and mortars," Table 3.
2. Nominal Blaine, cm²/g, of slags indicated 2 000, 3 000, 4 000, and 5 000.
3. NG indicates slag was not ground to this fineness.

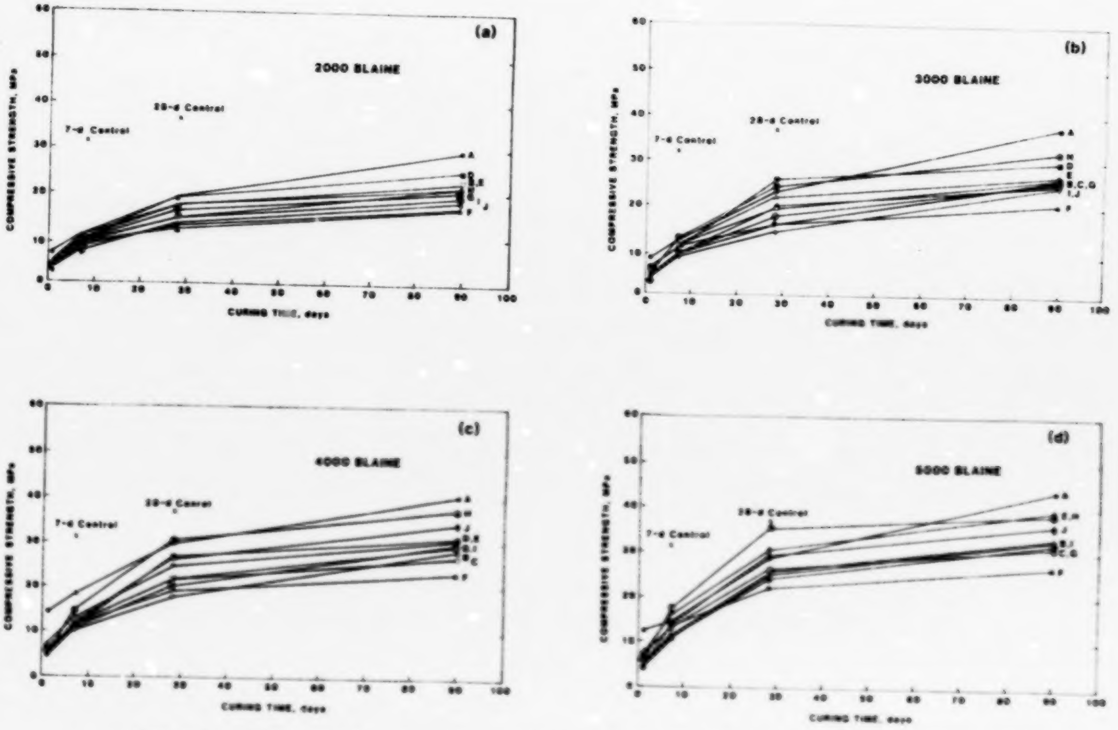

Fig. 3.5 — Compressive strength development at 23°C in moist-cured mortars containing 50% slag by absolute volume replacing portland cement (10)

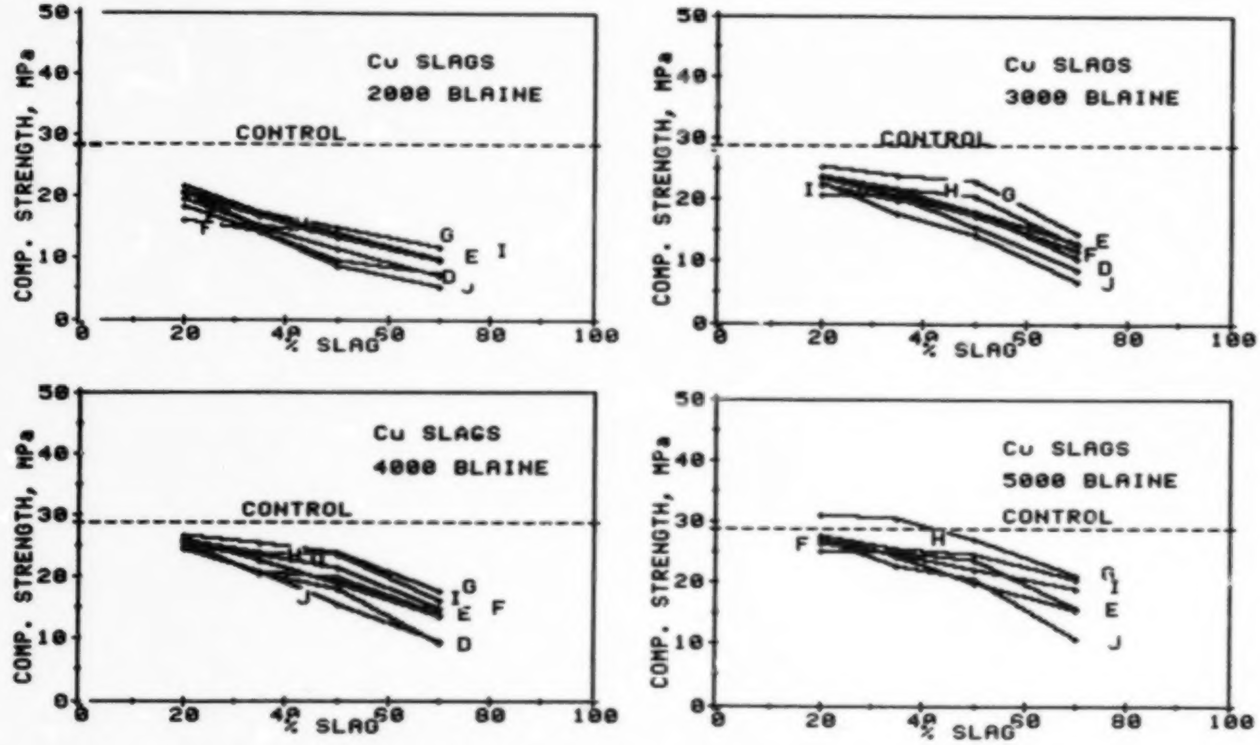

Fig. 3.6 — Compressive strength of copper slag–portland cement mortars at 28 days curing (10)

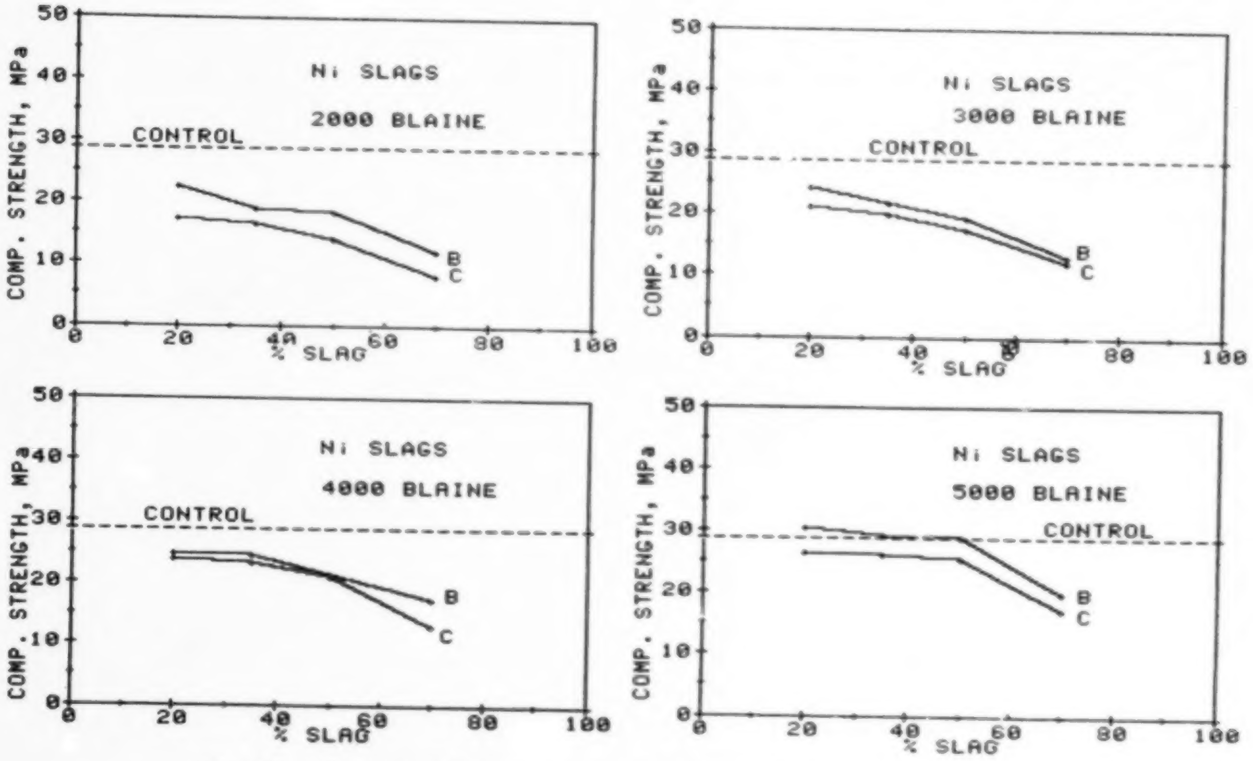

Fig. 3.7 — Compressive strength of nickel slag–portland cement mortars at 28 days curing (10)

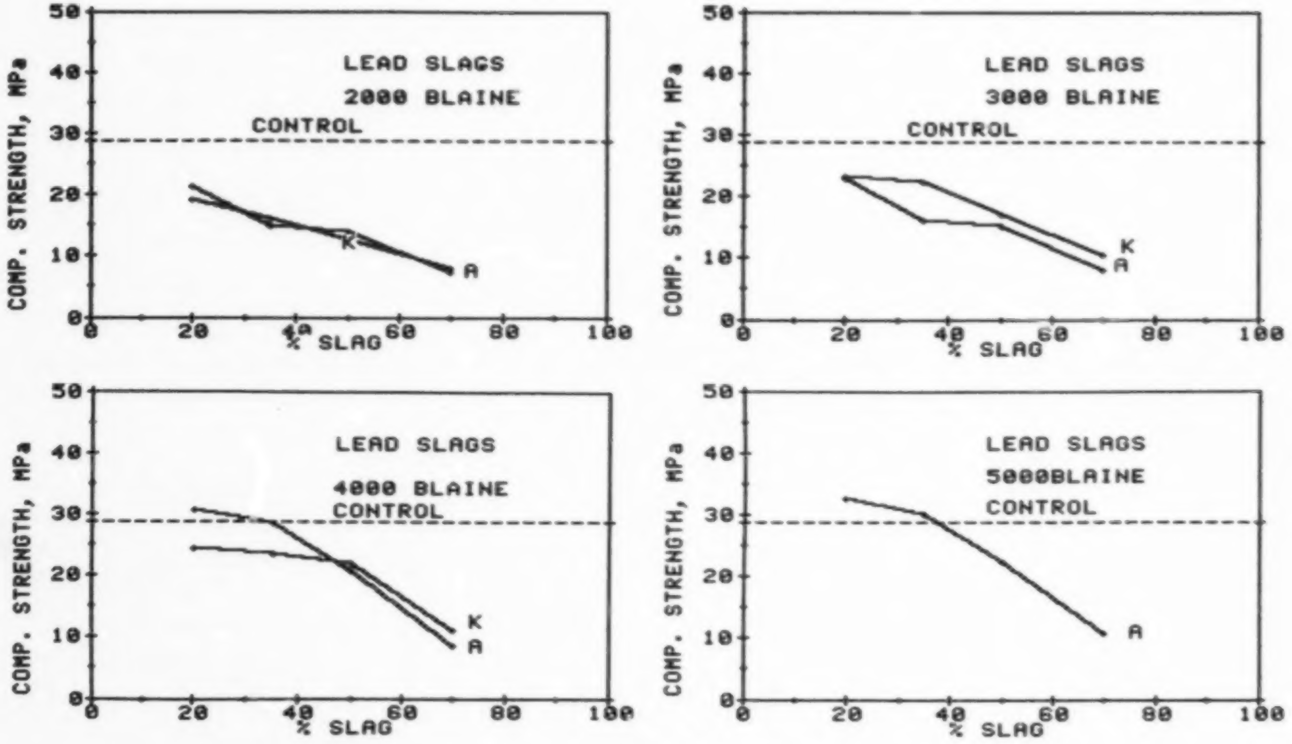

Fig. 3.8 — Compressive strength of lead slag-portland cement mortars at 28 days curing (10)

Table 3.7 — Chemical composition of air-cooled and of quenched nickel slags (Ontario) (17)

Slag description	Fe	S	SiO_2	CaO	MgO	Al_2O_3	$\%Al_2O_3 + \%CaO + \%MgO/\%SiO_2$ hydraulic modulus
Nickel reverberatory, air-cooled	36.0	1.5	35.5	2.25	2.50	5.05	0.2761
Nickel reverberatory, water-quenched	35.8	1.4	36.8	2.30	2.45	5.55	0.2799
Flash-furnace slag, air-cooled	35.8	1.5	30.8	7.00	2.45	6.00	0.5016
Flash-furnace slag, water-quenched	34.4	1.4	31.0	7.05	2.50	6.50	0.5177
Nickel reverb. + 14% limestone, water-quenched	32.9	1.4	32.8	9.40	2.45	5.85	0.5396
Ground quartz	0.58	—	87.7	0.27	0.029	1.10	0.0160

Table 3.8 — Composition of the specimens incorporating air-cooled and quenched nickel slags (Ontario) (17)

	Series No.						
Description	1	2	3	4	5	6	7
Wt % slag	0	0	1.2	4.5	4.5	8.7	16.0
Wt % cement	9.1	4.8	4.7	4.6	4.5	4.4	4.0
Wt % tailings	90.9	95.2	94.1	93.1	91.0	86.9	80.0
Total wt % binders	9.1	4.8	5.9	6.9	9.0	13.1	20.0
% cement replacement	0	0	20	33	50	66	80
Tailings/cement/slag	10:1:0	20:1:0	20:1:25	20:1:50	20:1:1	20:1:2	20:1:4

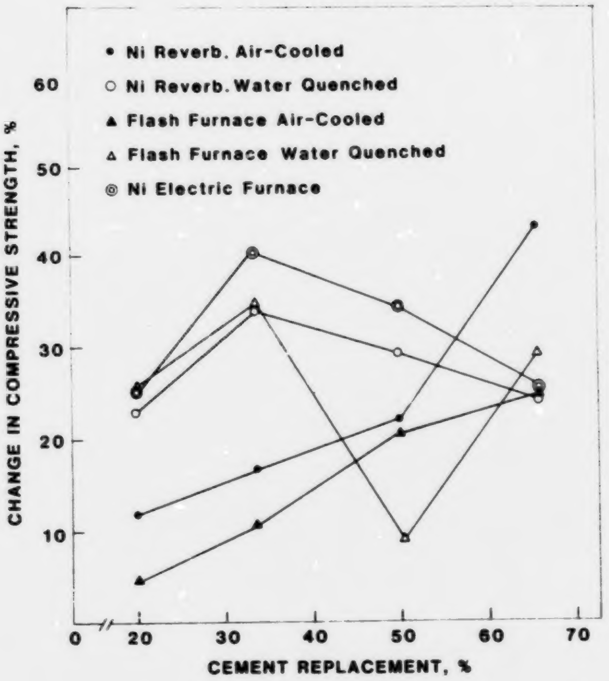

Fig. 3.9 — Change in strength at different curing ages calculated on basis of standard 4.8 wr % portland-cement specimens cured to same age during pozzolanic testing at various cement replacement levels (29)

Table 3.9 — Pozzolanic and slag activity indexes of portland cement–slag (Quebec) mortars cured at room temperature (21)

PI/HI*	Copper air-cooled	Copper quenched
2000	0.71/0.32	0.67/0.31
3000	0.73/0.36	0.87/0.27
4000	0.89/0.49	0.85/0.70
5000	0.91/0.38	1.06/0.52

*PI:pozzolanic index; HI:slag activity index (hydraulic index).

Table 3.10 — Pozzolanic and hydraulic indexes of Canadian non-ferrous slags (ASTM C 595) (21)

PI/HI	Lead (N.B.) granulated	Nickel (Ont.) air-cooled	Nickel (Ont.) quenched	Copper (Ont.) granulated	Copper (Ont.) quenched	Copper (Que.) air-cooled	Copper (Que.) air-cooled	Copper (Que.) quenched	Copper (Que.) granulated
2000	0.50/0.25	0.64/0.40	0.55/0.26	0.48/0.24	0.57/0.33	0.49/0.24	0.58/0.39	0.51/0.32	0.56/0.32
3000	0.54/0.27	0.73/0.43	0.67/0.41	0.69/0.29	0.72/0.43	0.67/0.35	0.80/0.49	0.73/0.42	0.70/0.40
4000	0.96/0.29	0.83/0.58	0.78/0.44	0.69/0.31	0.76/0.45	0.70/0.47	0.85/0.59	0.80/0.54	0.79/0.50
5000	1.01/0.36	0.98/0.67	0.88/0.57	NG	0.81/0.52	0.83/0.53	1.02/0.71	0.85/0.69	0.83/0.64

Notes:
1. Nominal Blaine fineness of slags indicated — 2 000, 3 000, 4 000, and 5 000.
2. NG indicates slag was not ground to this fineness.
3. PI and HI are the pozzolanic (pozzolanic activity index) and hydraulic (slag activity index), indexes with lime and cement, respectively, in accordance with ASTM C 595.

Effect of fineness on pozzolanic activity

Laneuville (5) evaluated the relative strength of mortars prepared in accordance with ASTM C 109, in which 30% of the cement was replaced by air-cooled nickel slag, ground to different finenesses. The strength of the test specimens was compared to that of a portland cement mortar at various curing ages (Table 3.11). *The experimental results indicate that compressive strengths are directly related to fineness*. Laneuville (5) also studied the effect of fineness on the hydraulic index at different curing ages (Fig. 3.10).

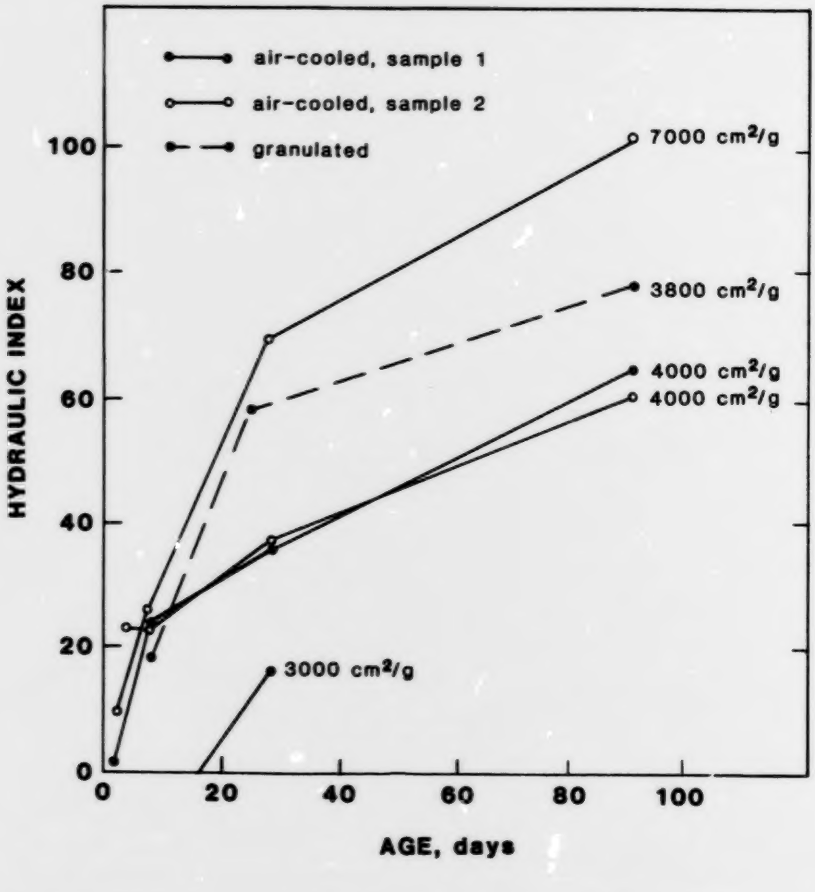

Fig. 3.10—Hydraulic index of air-cooled and of granulated nickel slags of different fineness (5)

The data indicate that granulated slags ground to 3 000 cm^2/g performed better than air-cooled slags ground to 4 000 cm^2/g. Nevertheless, air-cooled slags ground to 7 000 cm^2/g performed better than the rest of the slags (see Table 3.11). A more recent study indicates that the effect of fineness on the pozzolanic activity of Canadian copper, nickel, and lead slags, for both air-cooled and quenched samples, is directly related to pozzolanic activity as shown in Tables 3.9 and 3.10 (21).

Table 3.11 — Relative strength of portland cement–nickel slag mortars showing the effect of fineness (5)

Slag fineness, cm^2/g	Curing age, days	Relative strength, %
3000 (granulated)	3	63
	7	66
	28	81
4000 (air-cooled)	3	60
	7	72
	28	78
7700 (air-cooled)	3	68
	7	75
	28	90

4. HYDRATION OF NON-FERROUS SLAGS

Chemically, inorganic cementing materials derive from the multi-component system:

$$CaO–MgO–SiO_2–Al_2O_3–Fe_2O_3–SO_3$$

Portland cement, natural pozzolans, most fly ashes and many blast-furnace slags may generally be considered on a simplified ternary system $CaO–SiO_2–Al_2O_3$ with minor or insignificant amounts of MgO, SO_3, and Fe_2O_3, (see Fig. 2.1). Steel slags and non-ferrous slags are better represented by the system, $CaO–SiO_2–Fe_2O_3$, where CaO represents the sum of CaO, MgO, and Al_2O_3 (see Fig. 2.2).

Approximately 70 to 75 wt % of portland cement clinker is tricalcium silicate (C_3S) and β-dicalcium silicate (β-C_2S) with small amounts of Al_2O_3 and MgO dissolved in them (22). In addition, small amounts of calcium sulphate, usually in the form of gypsum, are added to portland cement clinker during the grinding operation for the purpose of controlling the initial hydration reactions.

Natural pozzolans of volcanic origin are composed of a vitreous phase of microporous texture with small amounts of a crystalline phase (23). The silica and alumina, that constitute the vitreous pyroclastic component, combined with lime in aqueous media yield insoluble cementitious products. The reactivity of pozzolans is determined not only by the structure, morphology, and chemical composition of the vitreous phase, but also by the fineness of the material (24), type and quantity of lime in the system (25,26) and water content (27).

Different hydration products have been identified on various pozzolan–$Ca(OH)_2$ systems. In some cases, C–S–H together with C_2ASH_8, or C–S–H, C_2ASH_8, hydrogarnet, and ($C_3A{\cdot}CaCO_3H_{12}$–C_4AH_{13}) were found, depending on the composition of the pozzolan. The CaO/SiO_2 ratio in the C–S–H is believed to be closely related to the concentration of Ca^{2+} in the solution (28).

The composition of slags depends on their origin. Copper slags analysed by scanning electron microscopy (SEM) (15) show that slags appear as intergrowths of fayalite, spinel, glass, and copper sulphides. Results of optical and SEM studies carried out in Spain (4) on granulated copper slags showed that the crystalline phase was composed mainly by needle-like fayalite (Fe_2SiO_4) and globular iron oxides.

Not much is known about the composition of other slags. It might be expected that materials as diverse as portland cement, pozzolans, and ferrous and non-ferrous slags would react with water to form markedly different compounds. In practice, there is a remarkable similarity in the reaction products from these materials. The common factor in all of these systems is the ultimate formation of C–S–H and the correspondence between its formation and the development of structural bonds in the hydrating mass.

Kam (29) studied the hydration of copper reverberatory-furnace slag in the presence of $Ca(OH)_2$, $CaCO_3$, and portland cement. The experimental analysis of the hydration products comprised measurements of early heat of hydration, determination of non-evaporable water in the reaction products, quantitative X-ray diffraction analysis, and scanning electron microscopy.

Kam reported that the rate of heat evolution decreased as the proportion of slag increased. Also, the amount of non-evaporable water increased as the amount of slag in the paste increased. Kam's studies also showed an unidentified diffraction peak at 7.34 Å in the X-ray diffractograms for all the hydrated slag–$Ca(OH)_2$ pastes. The X-ray diffraction study showed also that the fayalite crystals do not take part in the hydration reactions. Such reactions are limited to the glass phase.

Roper et al. (16) reported that copper reverberatory-furnace slag need not be completely glassy for significant hydration to occur. Recent investigation by Douglas et al. (15) on an air-cooled copper slag with 41% glass and on a quenched copper slag with 95% glass, showed that the presence of the slag delays the transfer of Ca^{2+} from the portland cement constituents to the solution at the early stage of hydration.

In the later stage, between 24 and 72 hours of hydration, the measured Ca^{2+} concentration in the solutions in contact with the binders and the percentage of $Ca(OH)_2$ in the solid phase at the same age suggest that more C_3S from the portland cement had reacted in the slag blend than in the portland cement paste. Although the study showed that air-cooled slags may outperform quenched slags, depending on the fineness, further research in this area is needed.

5. STRENGTH DEVELOPMENT OF MINE BACKFILL MATERIAL INCORPORATING NON-FERROUS SLAGS

Most of the studies intended to encourage the use of copper, nickel, and lead slags have been directed toward exploring the feasibility of their use as cement replacement in cemented mine backfill. Strength development of copper reverberatory-furnace slag, de-zinced lead smelter slag, and copper converter slag in cemented fill were first studied by Thomas (3,6) in Australia and his data are shown in Figures 3.2 and 3.3.

Kam in a recent study (29) showed that significant strength could be developed with slag–$Ca(OH)_2$ mixes, where higher $Ca(OH)_2$ content would lead to higher strength (Table 5.1). Strength development, equivalent to that obtained with portland cement–slag mixes, can be achieved with cemented fill using copper reverberatory-furnace slag and lime mixtures (29). Variations in the strength of fill at early ages are mostly affected by density and water content (Table 5.2), both of which are related to consolidation conditions.

Table 5.1 — Uniaxial compressive strength of ground copper reverberatory-furnace slag and $Ca(OH)_2$ pastes (29) (Water/solids ratio = 0.30)

CRFS*:$CA(OH)_2$	Strength, MPa	Mean, MPa	Standard deviation, MPa
1:1	6.632 3.314 5.834 7.622	5.851	1.842
2:1	4.678 4.882 4.540 4.642	4.686	0.143

*CRFS: copper reverberatory-furnace slag.

At later ages, variations in strength are affected by the amounts of hydrated cementitious materials in the mix. Improvement in compaction methods of backfill in stopes should be an important goal, if early strength development is required. According to Kam (29), increased compaction could be achieved by rapid drainage of the wet fill as it is being placed, and vibration methods should also be explored. Changes in the grain size distribution of the fill materials, such as rejected slimes, may improve the particle size distribution and therefore the compaction of the fill material.

Table 5.2 — Effect of density and water content on compressive strength of fill at an early age (24)

Dry density, g/cm³	Water content, g	Strength, MPa
2.21	29.7	2.028
2.10	12.3	1.596
2.10	15.2	1.331
2.18	13.5	1.852
2.17	12.6	1.869
1.96	16.3	0.926
2.13	13.8	1.719
2.23	11.9	1.772
2.15	13.3	1.640
2.18	12.6	1.940
2.20	13.2	2.134
2.10	15.5	1.667

A recent study by Emery (21) reports tests at 7, 28, and 90 days on a granulated copper slag from Ontario and on a remelted and quenched copper slag from Quebec in mixes with mine tailings (Tables 5.3 and 5.4). Measurements were made on 50-mm uncompacted cubes containing 70% mine tailing. The cubes were demolded when sufficient strength was obtained; they were stored in the moist room at 23°C; after 28 days the specimens were tested for compressive strength. It was found that little improvement in strength developed in the cementitious systems with 12 wt % slag and 4% portland cement, compared with the blend of 4 wt % slag and 4% portland cement.

A decrease in compressive strength between 28 and 90 days was also reported. It would appear that most of the cementitious properties were due to the portland cement and that lower compressive strength at 90 days may be related to the components in the tailings causing chemical reactions during curing. It is doubtful that this will be a factor in actual applications.

Table 5.3 — Mix proportions for cemented-mine tailings and compressive strength development (21)

Mix	Mix No. 1 slag	Mix No. 2 slag	Mix No. 3 slag
Compressive strengths, MPa			
7 days (strength not adequate for testing)	—	—	—
28 days	2.2	2.3	2.5
	2.1	2.1	2.4
	1.9	2.3	2.5
Average	2.1	2.2	2.5
90 days	1.63	1.62	1.66
	1.66	1.68	1.68
	1.59	1.67	1.69
Average	1.63	1.66	1.68
Slag 4000 Blaine, kg	0.100	0.232	0.300
Type 10 cement, kg	0.100	0.116	0.100
NRT tailings, kg	2.300	2.552	2.100
Water, kg	0.750	0.870	0.750

Note: Absolute volume replacement not adopted.
Mix No. 1: 4% slag 4000 Blaine and 4% Type 10 portland cement.
Mix No. 2: 8% slag 4000 Blaine and 4% Type 10 portland cement.
Mix No. 3: 12% slag 4000 Blaine and 4% Type 10 portland cement.

Table 5.4 — Cemented rockfill mix proportions and compressive strength development of rockfill (21)

	Compressive strengths, MPa
7 days	
(Strength not adequate for testing)	
28 days	1.04
	1.14
	0.88
Average	1.02
90 days	1.59
	1.88
	1.72
Average	1.73
Mix proportions	
KCCG 3000, kg	3.27
ASTM Type 10 cement, kg	2.18
Fine rockfill, kg	27.27
Coarse rockfill, kg	81.82
Water, kg	5.46

Notes: 1. Some places of segregation observed for test cylinders.
2. Absolute volume replacement not adopted.

6. STRENGTH DEVELOPMENT OF MORTARS AND CONCRETE INCORPORATING NON-FERROUS SLAGS

Tests for strength development of mortars incorporating non-ferrous slag binders have been conducted by Laneuville (5) and by Baragano (4) using nickel and copper slags. Reports of research on the use of lead slags as partial portland cement replacement in steam-cured blocks have been published recently (7). The specimens were made with ground lead slags and calcium-bearing materials such as lime, gypsum, and portland cement. Mixtures had been prepared consisting of three parts of sand and one part of a binder formed by different combinations of ASTM Type III portland cement and a lead slag ground to 2 500 cm²/g. The results showed that up to 25 wt % ground slag can replace cement before significant strength loss occurs (Fig. 6.1).

Tests on strength development of mortars, some incorporating air-cooled, granulated and quenched lead, nickel, and copper slags from Canadian sources, have been reported and data are shown in Table 5.3 (21). Portland cement in the mortar was replaced by the slag. The mortars were cured at 38°C for 28 days. Higher strengths were observed in air-cooled than in quenched nickel slags. Strengths of granulated copper slag from Ontario were slightly improved by adding 20% CaO to the melted slag and by quenching in excess water.

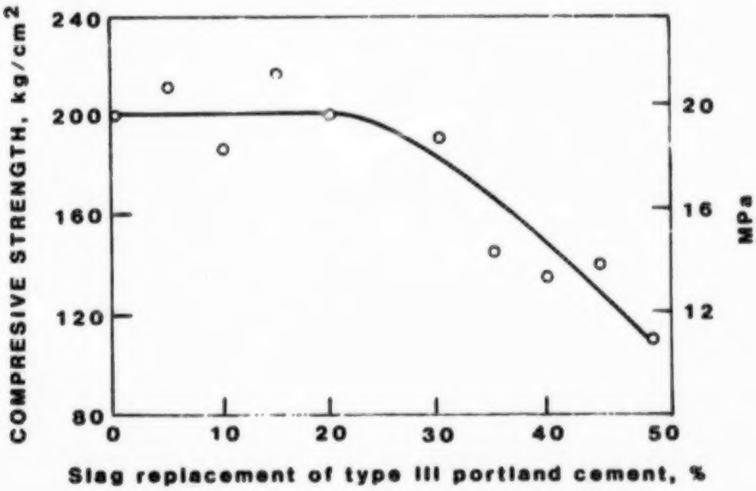

Fig. 6.1 — Compressive strength of Type III portland cement–lead slag binders at various cement replacement levels (7)

Table 6.1 — Compressive strength at 28 days (MPa) of mortar cubes cured at 38°C with 20, 35, 50, and 70% absolute replacement of portland cement by slag (21)

	Lead (N.B.) granulated	Nickel (Ont.) air-cooled	Nickel (Ont.) quenched	Copper (Ont.) granulated	Copper (Ont.) quenched	Copper (Que.) air-cooled	Copper (Que.) air-cooled	Copper (Que.) quenched	Copper (Que.) granulated
CONTROL	29.6	29.6	29.6	29.6	29.6	29.6	29.6	29.6	29.6
20%									
2000 BLAINE	21.4	22.5	17.1	16.0	20.7	20.8	21.7	19.3	20.2
3000	22.7	24.0	20.9	23.4	23.6	22.1	25.2	23.9	20.6
4000	30.5	24.8	23.8	25.4	25.8	24.6	26.5	25.7	24.6
5000	32.3	30.2	26.3	NG	27.5	25.0	30.8	27.6	26.2
35%									
2000 BLAINE	14.7	18.9	16.4	14.2	17.0	14.6	17.2	15.1	16.6
3000	16.1	21.5	19.7	20.4	21.3	19.8	23.7	21.5	20.8
4000	28.5	24.5	23.0	20.3	22.5	20.8	25.3	23.8	23.5
5000	30.0	29.1	25.9	NG	24.1	24.6	30.3	25.3	24.3
50%									
2000 BLAINE	13.7	18.3	13.9	9.5	13.8	11.3	14.6	13.4	13.3
3000	15.0	19.1	17.3	15.5	18.0	18.0	22.7	20.2	17.3
4000	20.6	21.4	20.9	17.8	18.8	19.7	23.9	23.6	21.3
5000	22.3	28.7	25.4	NG	19.6	23.3	26.9	24.4	22.0
70%									
2000 BLAINE	7.3	11.9	7.8	7.2	9.7	7.0	11.5	9.7	9.6
3000	7.9	12.8	12.1	8.5	12.8	10.5	14.5	12.5	11.7
4000	8.5	17.1	13.0	9.1	13.4	13.9	17.5	16.0	14.7
5000	10.8	19.8	16.8	NG	15.5	15.6	21.0	20.4	18.8

Notes: 1. Portland cement meets requirements of CSA Type 10.
2. Nominal Blaine fineness of slags indicated — 2 000, 3 000, 4 000, and 5 000.
3. All compressive strengths in MPa.
4. NG indicates slag was not ground to this fineness.

Table 6.2 — Compressive strength at 23°C (MPa) of mortar cubes with 50% absolute volume replacement of portland cement by slag (21)

	Lead (N.B.) granulated	Nickel (Ont.) air-cooled	Nickel (Ont.) quenched	Copper (Ont.) granulated	Copper (Ont.) quenched	Copper (Que.) air-cooled	Copper (Que.) air-cooled	Copper (Que.) quenched	Copper (Que.) granulated
CONTROL 7D	31.3	31.3	31.3	31.3	31.3	31.3	31.3	31.3	31.3
28D	36.8	36.8	36.8	36.8	36.8	36.8	36.8	36.8	36.8
2000									
days 1 BLAINE	7.0	3.9	4.8	4.6	4.7	3.1	3.3	4.3	3.8
7	10.8	8.7	10.7	9.0	9.1	8.8	9.2	9.3	7.4
28	19.1	14.2	17.8	19.0	17.0	12.0	14.4	16.2	13.8
90	29.5	21.6	23.0	25.1	21.7	16.7	19.4	21.1	18.5
3000									
days 1 BLAINE	8.5	4.0	5.0	4.9	5.0	4.7	3.3	5.0	4.0
7	12.4	8.8	10.8	10.3	11.0	10.9	9.5	12.6	8.6
28	23.5	15.6	19.3	25.7	21.8	15.7	18.0	24.6	14.3
90	37.9	26.0	26.1	29.7	26.5	20.6	25.9	32.0	24.3
4000									
days 1 BLAINE	12.1	4.1	5.2	5.6	6.3	5.0	4.3	5.6	4.7
7	14.1	10.0	11.7	10.5	12.5	12.0	11.0	14.8	10.3
28	29.8	17.5	21.7	26.7	24.8	19.2	20.5	30.5	21.6
90	40.2	28.3	26.6	31.4	31.1	23.2	29.2	37.3	29.1
5000									
days 1 BLAINE	14.1	4.4	7.0	NG	7.5	5.1	4.5	5.9	5.3
7	16.2	11.2	13.1		16.0	12.9	11.2	17.1	11.5
28	28.7	25.0	26.2		30.4	21.3	24.2	35.2	25.9
90	43.7	33.1	31.7		38.9	26.8	32.0	38.3	32.8

Notes: 1. Portland cement meets requirements of ASTM "Specifications for ground blast-furnace slag for use in concrete and mortars."
2. Nominal Blaine fineness of slags indicated — 2 000, 3 000, 4 000, and 5 000
3. All compressive strengths in MPa, with flow indicated for each mix
4. NG indicates slag was not ground to this fineness

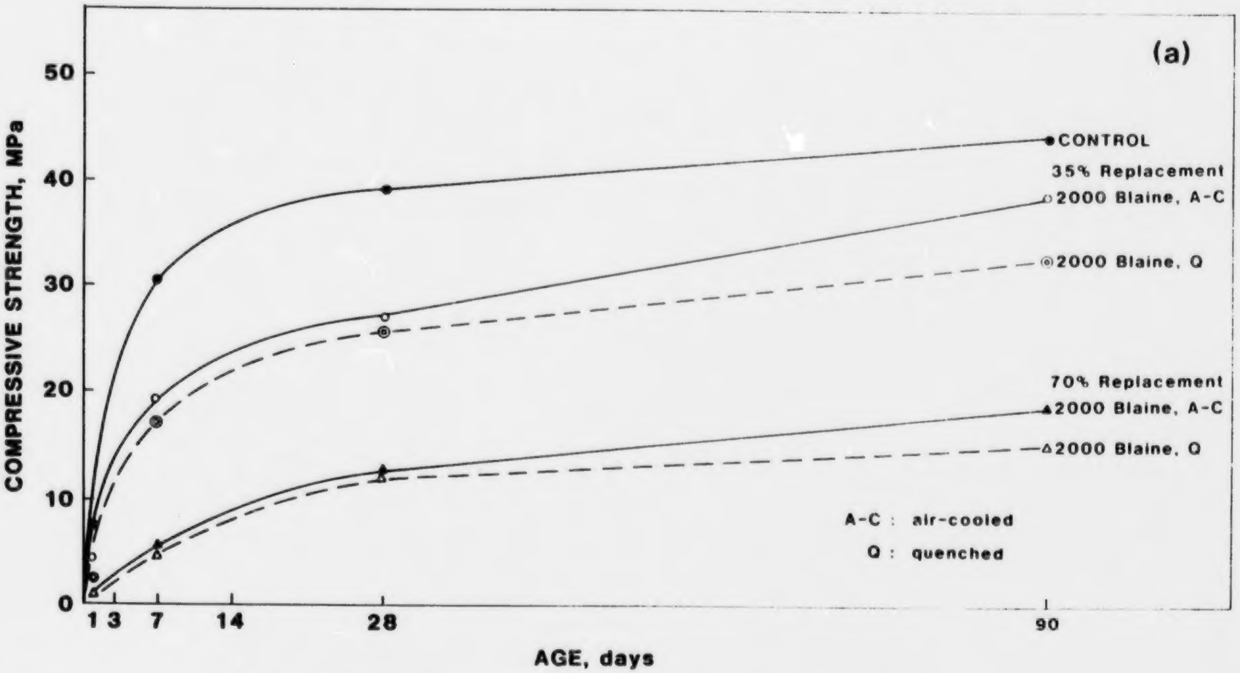

Fig. 6.2.a — Strength development in portland cement–copper slag mortars cured at room temperature (15). Slag ground to 2000 cm^2/g

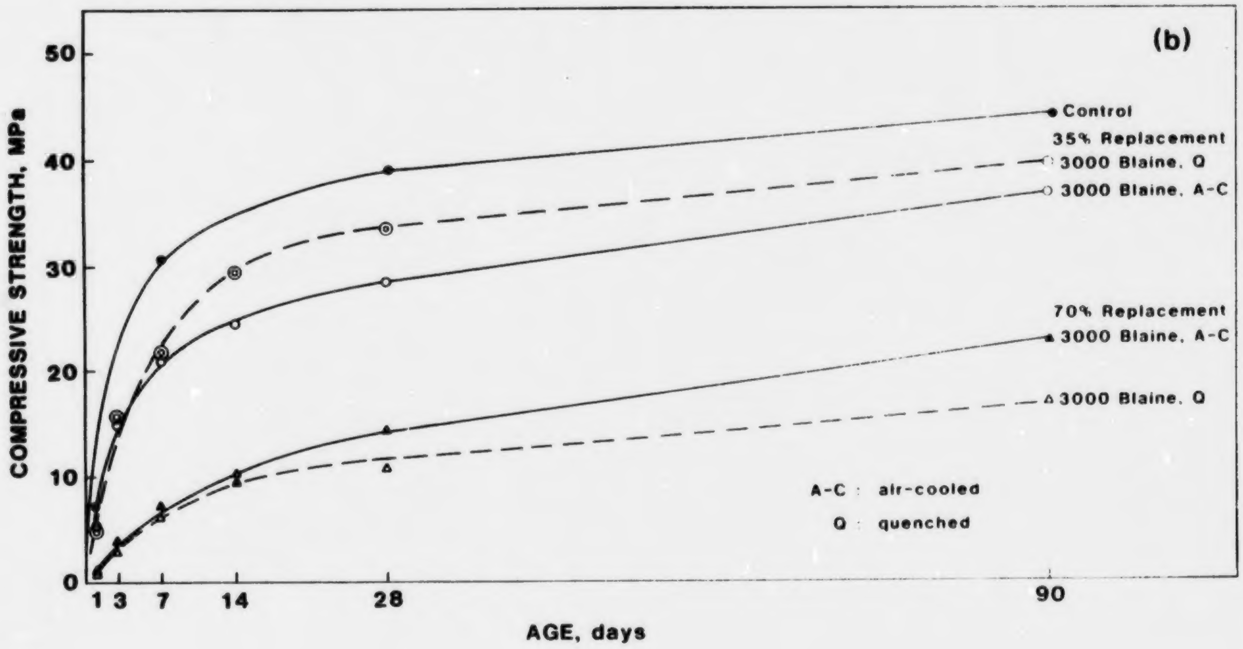

Fig. 6.2.b — Strength development in portland cement–copper slag mortars cured at room temperature (15). Slag ground to 3000 cm²/g

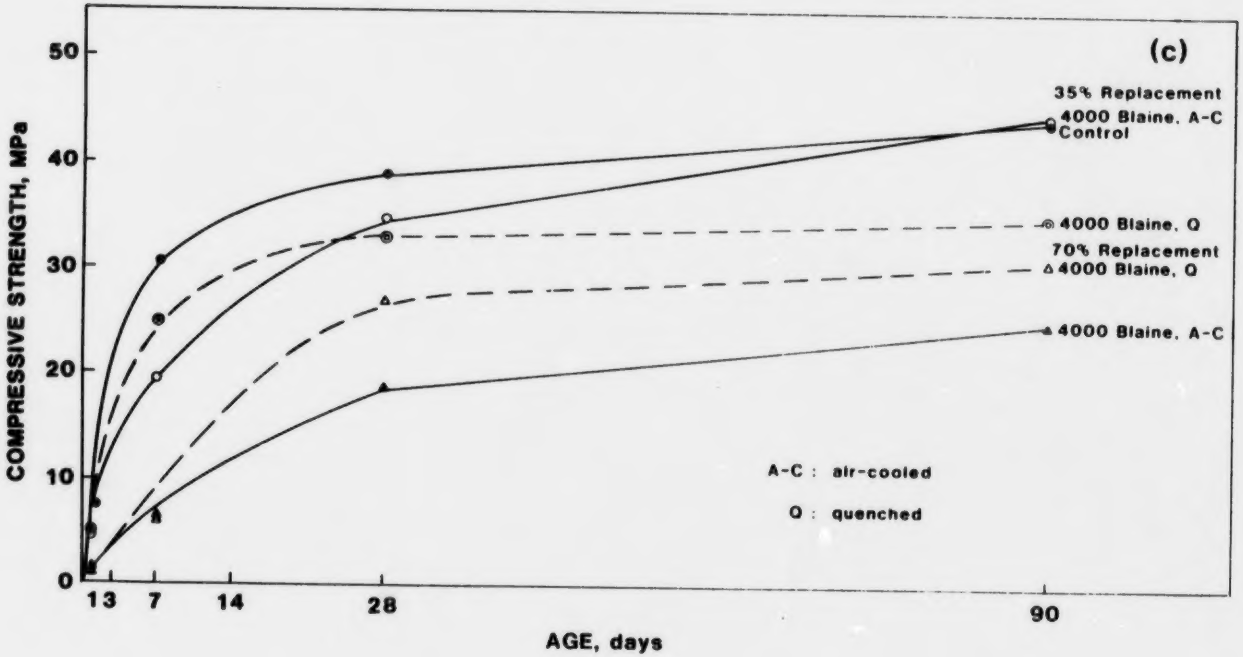

Fig. 6.2.c — Strength development in portland cement–copper slag mortars cured at room temperature (15). Slag ground to 4000 cm²/g

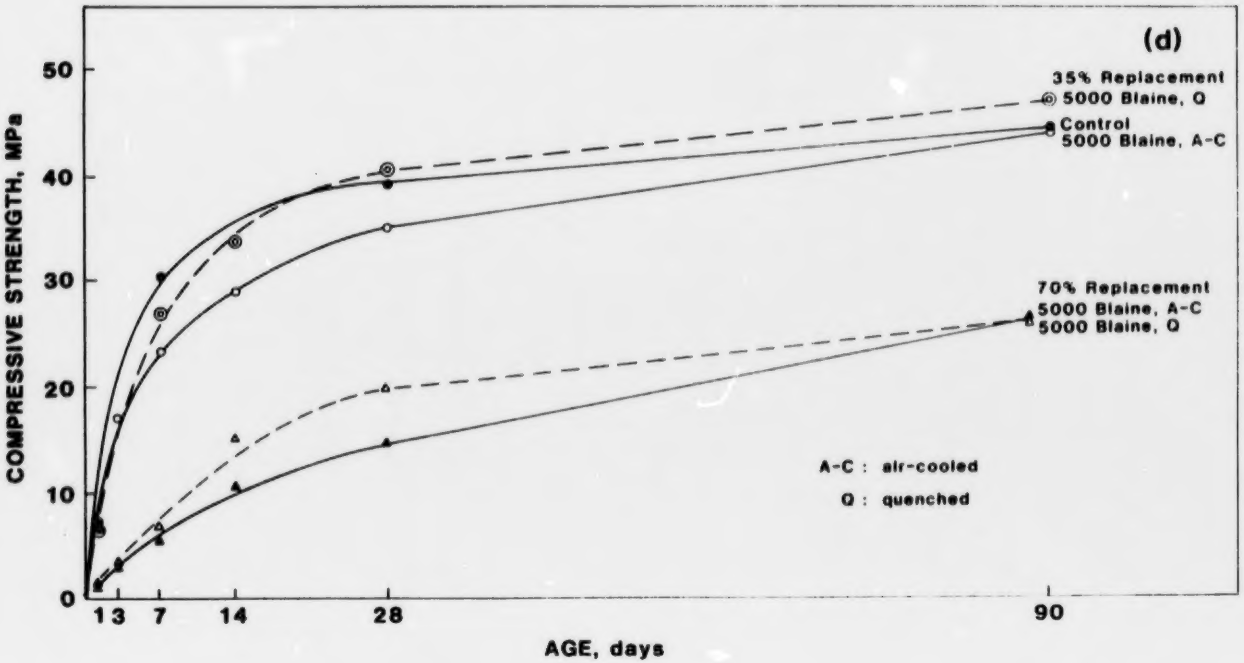

Fig. 6.2.d — Strength development in portland cement–copper slag mortars cured at room temperature (15)

Investigations by Emery (21) show that air-cooled copper reverberatory-furnace slag from Quebec exhibited higher strengths than the quenched slag from the same source at the same fineness in some of the specimens; some of his data are shown in Table 6.1. Another series of tests was performed with mortars in which 50% of the portland cement had been replaced by the slag (21). The mortars were cured at room temperature (23°C) and were tested at 1, 7, 28, and 90 days (Table 6.2). The results show that several slags appear to have portland cement replacement potential at the 4 000 Blaine level.

Douglas and Mainwaring (15) have reported strength development of mortars of portland cement–copper slags binders with 35 and 70% cement replacement. The mortars had been placed in close-fitting containers stored at 23 ± 1.7°C and had been tested at 1, 7, 28, and 90 days (Fig. 6.2.a to 6.2.d).

The compressive strength of mortar incorporating 35% of air-cooled slag ground to 4 000 cm^2/g (Blaine method) was higher than that of a mortar incorporating 35% of the quenched slag with the same fineness. At 90 days the strength of the former attained that of the portland cement mortar used as a control. In mortars with 70% replacement, the mortar incorporating the quenched slags developed higher strength than that incorporating the air-cooled slag.

Other recent studies on Canadian non-ferrous slags showed that some slags ground to 4 000 cm^2/g outperform the corresponding 3 000-cm^2/g materials. However, many of the 3 000-cm^2/g materials are sufficiently reactive to save the extra grinding costs (11).

Details of a recent study on concrete mixes, incorporating Canadian ground non-ferrous slags have been reported (21), and their compressive strength development are shown in Tables 6.3, 6.4, and 6.5 . Table 6.5 shows the effect of a water-reducing admixture on compressive strength development at different ages. Tables 6.4 and 6.5 allow comparison of the concrete mixes incorporating ground non-ferrous slags in terms of both compressive strength development at 7, 28, and 90 days, and compressive strength ratio to the control at the same ages.

Figure 6.3 shows compressive strength development, and Figure 6.4 the compressive strength ratio. Evidently the compressive strengths of concrete mixes incorporating lead slag at 90 days is equivalent to the compressive strength of the control at 28 days.

Effect of Glass Content on Strength Development

Limited information is available on the relationship between glass content and strength development with time for portland cement concrete incorporating non-ferrous slag. Results on strength development of non-ferrous slag binders, both air-cooled and quenched, were reported in a Canadian patent (5). Mortars made with 70:30 cement-to-slag ratio were tested for compressive strength (ASTM C 109). Nickel slags were used; air-cooled slags were ground to a specific surface of 4 000 cm^2/g, the granulated slags to 3 800 cm^2/g. Results to 90 days of curing indicated that water-quenching improved the long-term strength of glassy nickel slag binders.

Douglas et al. (30) have reported tests on strength development of mortars (ASTM C 109) incorporating air-cooled, granulated, and quenched lead, nickel, and copper slags from Canadian sources. With each test, a different amount of portland cement in the mortars was replaced by the slags. The mortars were cured at 38°C for 28 days. Higher strengths were observed in air-cooled than in quenched copper slags (see Fig. 6.2). Strengths of granulated copper slag from Ontario were slightly improved by adding 20% CaO to the melted slag and by quenching in excess water. Air-cooled copper reverberatory-furnace slag from Quebec exhibited higher strengths than the more glassy quenched slag from the same source in some of the specimens.

Another series of tests was performed with mortars (ASTM C 109) in which 50% of the portland cement was replaced by the slag (31). The mortars were cured at room temperature (23°C) and tested at 1, 7, 28, and 90 days (see Table 6.2). The results show that some slags ground to 4 000 cm^2/g and cured at 90 days outperformed the control specimens.

Table 6.3 — Gradations of coarse and fine aggregates for concrete mixes (21)

	Sieve size	Per cent passing	CSA A23.1 requirements per cent passing
Coarse aggregate	25.4 mm	100	100
	19 mm	95	90–100
	12.7 mm	52	30–75
	9.5 mm	36	20–55
	4.75 mm	2	0–10
Fine aggregate	9.5 mm	100	100
	4.75 mm	97	95–100
	2.36 mm	85	80–100
	1.18 mm	72	50–85
	600 µm	52	25–60
	300 µm	22	10–30
	150 µm	6	2–10

Table 6.4 — Compressive strength development of concrete mixes containing 50% ground non-ferrous slags incorporated by absolute volume replacement (21) of CSA Type 10 portland cement

Mix	A	A	B	D	D	E	G	G
BLAINE	3000	4000	3000	4000	3000	4000	3000	3000
Mix details								
Ground non-ferrous Slag, kg	8.32	8.32	7.36	7.36	8.09	8.09	7.04	7.31
Type 10 cement, kg	6.54	6.54	6.54	6.54	6.54	6.54	6.04	6.54
Fine aggregate, kg	38.41	38.41	38.41	38.41	38.41	38.41	35.54	38.41
Coarse aggregate, kg	52.86	52.86	52.86	52.86	52.86	52.86	48.96	52.86
Water, kg	7.28	7.28	6.82	6.82	7.17	7.17	6.41	6.80
WRA, mL	—	—	—	—	—	—	—	—
Slump, mm	130	130	75	75	110	120	50	70
Air, %	1.5	1.5	2.2	1.9	1.5	1.9	1.7	1.5
Temperature, °C	20	19	20	20	20	20	20	20
Bulk density, kg/m³	1937	1963	1949	1923	1958	1953	1937	1958
Compressive strengths, MPa								
7 days	9.5 9.3 10.0	12.4 11.9 12.1	9.2 9.2 9.7	10.7 10.2 10.7	9.9 9.4 9.5	10.2 11.1 10.4	10.7 10.5 10.7	9.7 9.6 9.4
Average	9.6	12.1	9.4	10.5	9.6	10.6	10.6	9.6
28 days	23.7 21.4 21.7	28.5 27.3 30.3	16.8 17.3 16.8	20.1 20.4 20.9	22.4 22.4 21.9	24.7 24.7 26.0	21.4 21.7 21.2	17.3 19.4 18.4
Average	22.2	28.7	17.0	20.5	22.2	25.1	21.4	18.4
90 days	32.6 35.6 35.7	40.8 39.7 42.8	23.4 24.0 22.9	28.5 28.0 27.0	28.0 28.0 27.5	28.5 30.1 29.6	31.6 30.1 31.1	24.5 25.5 24.5
Average	34.6	41.1	23.4	27.8	27.8	29.4	30.9	24.8

Note: All mixes and test in accordance with CSA A23.1 and CSA A23.2, respectively. 100 × 200-mm cylinders for all mixes except Control 1 (150 × 300-mm cylinders).

Table 6.5 — Compressive strength development of concrete mixes containing 50% ground non-ferrous slags incorporated by absolute volume replacement of Type 10 portland cement, with water-reducing admixtures (WRA) (21)

Mix	B	B	C	C	F	G
Mix details	3000 WRA	4000 WRA		WRA	4000 WRA	3000 WRA
Ground non-ferrous slag, kg	7.36	7.36	7.14	7.14	7.77	7.32
Type 10 cement, kg	6.54	6.54	6.54	6.54	6.54	6.54
Fine aggregate, kg	38.41	38.41	38.41	38.41	38.41	38.41
Coarse aggregate, kg	52.86	52.86	52.86	52.86	52.86	52.86
Water, kg	6.46	6.46	6.46	6.46	6.46	6.46
WRA, mL	64.5 (TCDA A)	64.5 (TCDA A)	—	63.5 (Mulco A)	66.4 (Mulco A)	64.3 (TCDA A)
Slump, mm	110	90	40	90	90	90
Air, %	4.0	3.3	2.5	5.3	3.3	3.7
Temperature, °C	21	21	20	22	21	21
Bulk, density, kg/m³	1967	1936	1954	1913	1937	1967
Compressive strengths, MPa						
7 days	12.2	12.0	14.8	14.8	15.0	11.2
	12.2	11.7	13.8	14.8	14.5	11.7
	11.7	12.4	13.8	14.0	14.8	11.7
Average	12.0	12.0	14.1	14.5	14.8	11.5
28 days	21.4	24.5	22.9	24.0	23.4	22.9
	21.9	24.5	22.4	23.2	24.0	24.0
	21.4	25.0	23.4	22.9	23.4	24.0
Average	21.6	24.7	22.9	23.9	23.6	23.6
90 days	30.6	31.1	31.1	30.1	27.8	30.6
	29.6	31.6	30.1	31.1	28.8	31.6
	29.1	21.1	20.1	31.2	28.3	31.7
Average	29.8	31.3	30.4	30.8	28.3	31.3

Note: All mixes and tests in accordance with CSA A23.1 and CSA A23.2, respectively, 100 × 200-mm cylinders.

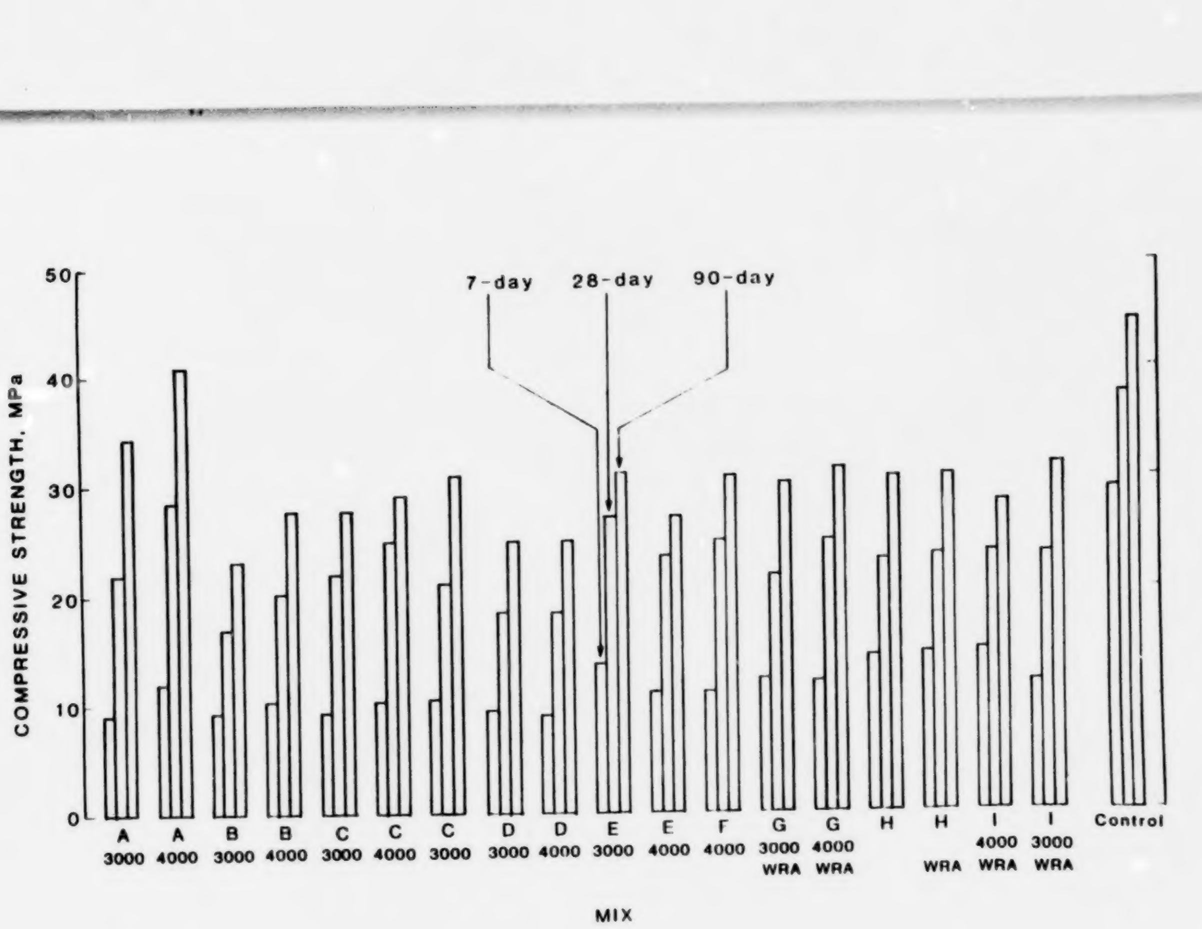

Fig. 6.3 — Compressive strengths of concrete mixes (21)

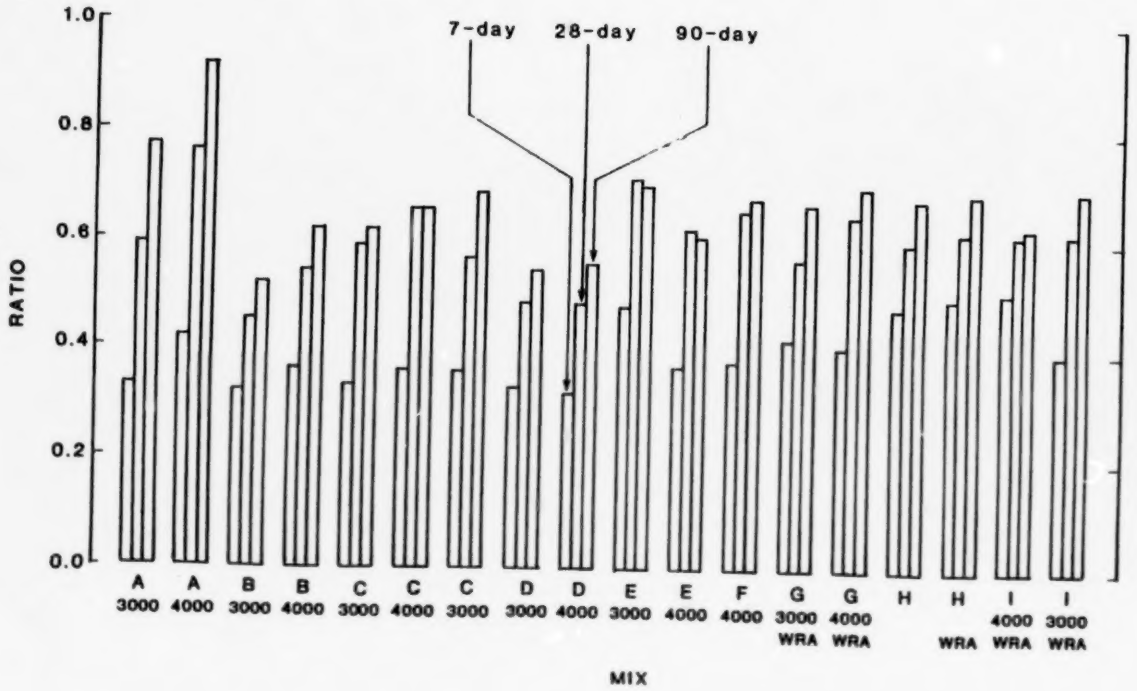

Fig. 6.4 — Compressive strength ratios of concrete mixes (21)

Strength development in mortars of portland cement–copper slag binders with 35 and with 70% cement replacement was recently reported by Douglas and Mainwaring (15). The mortar cubes (ASTM C 595) were tested at 1, 7, 28, and 90 days (Fig. 6.5). The compressive strength of mortar incorporating 35% of air-cooled slag ground to 4 000 cm^2/g (Blaine method) was higher than that of a mortar incorporating 35% of the more glassy quenched slag. At 90 days the strength of the former attained that of the portland-cement mortar used as control.

Effect of Fineness on Strength Development

Improved strengths of finer granulated blast-furnace slags reported in the literature (32) led some investigators to study the effect of fineness in strength development of nickel slag binders (5). Compressive strength data were reported on mortars (ASTM C 109) containing 70% portland cement and 30% air-cooled nickel slag. The mortars were cured in water at 23°C. An increase of about 15% in compressive strength after 90 days was observed for specimens made with slags ground to 4 000 cm^2/g, compared to those slags ground to 3 000 cm^2/g.

Data on mortars made with an air-cooled nickel slag of similar chemical composition but with a MgO content 2% higher than in the first sample were also reported (5). Strength development of the two air-cooled slags was about the same when ground to a specific surface of 4 000 cm^2/g. Increasing the specific surface to 7 700 cm^2/g resulted in about 15% increase of compressive strength at 90 days. Strength development of mortars incorporating air-cooled nickel slag ground at different fineness and cured at 23°C are shown in Figure 6.6 (5). Compressive strengths at 28 days of mortars incorporating lead, nickel, or copper slags ground to 2 000, 3 000, 4 000, and 5 000 cm^2/g were reported in Canada (see Table 6.2) (29).

Effect of Slag Content on Strength Development

Apparent discrepancies have been reported on the effect of slag content on the strength development of nickel slag binders. Thomas (33) found increasing strength in mixes of tailings with a fixed amount of portland cement and copper slag content about double that of cement.

Laneuville (34) reported negligible contribution of a granulated nickel slag to early age strength and a progressively greater contribution after 90 days of wet-curing at 21°C for binders containing less than 45% slag (Fig. 6.7).

The discrepancy between the two sets of results, those of Thomas and those of Laneuville, was explained by Laneuville in terms of the decreasing ratio of water to cementitious materials when larger amounts of slag are added to a constant amount of portland cement. Measurements of the combined water in mortars of slag binders showed a direct relationship between compressive strength and combined water (Fig. 6.8).

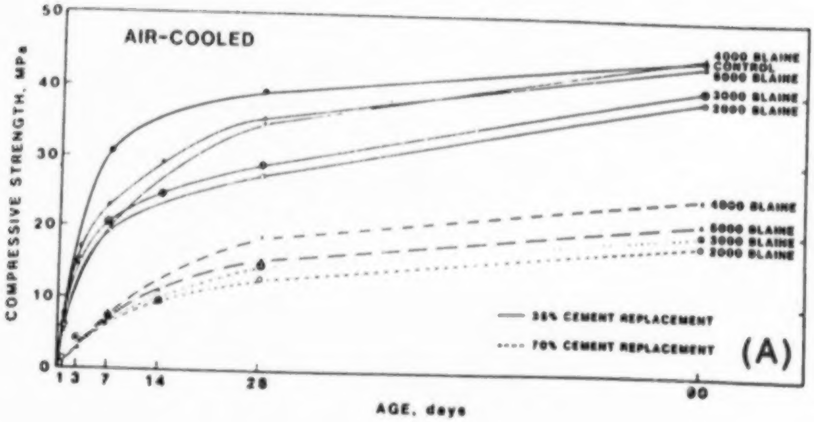

Fig. 6.5.a — Strength development in portland cement–slag mortars with 35 and 70% air-cooled slag replacing cement.

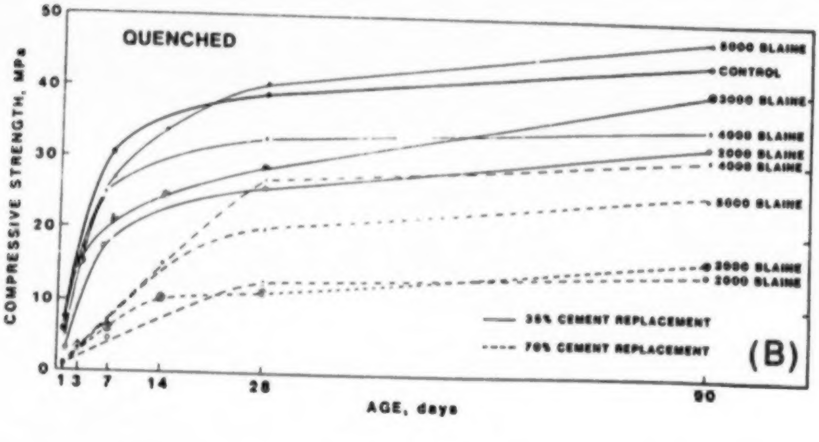

Fig. 6.5.b — Strength development in portland cement–slag mortars with 35 and 70% quenched slag replacing cement.

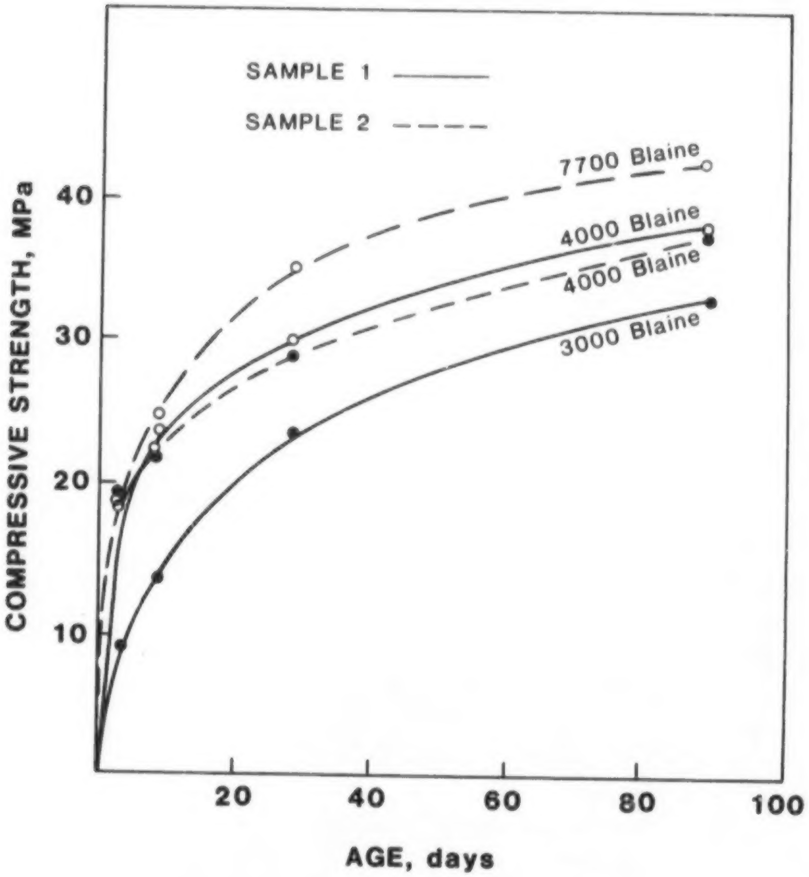

Fig. 6.6 — Effect of fineness on compressive strength of 70 wt % portland cement and 30 wt % air-cooled nickel slag binders (5)

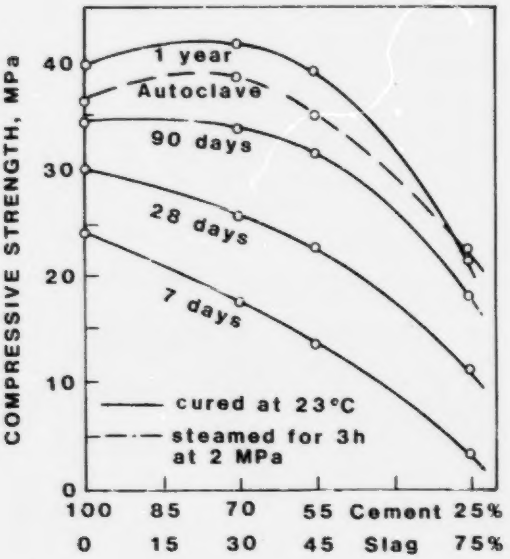

Fig. 6.7 — Effect of slag content of binders on compressive strength of mortar cubes (34)

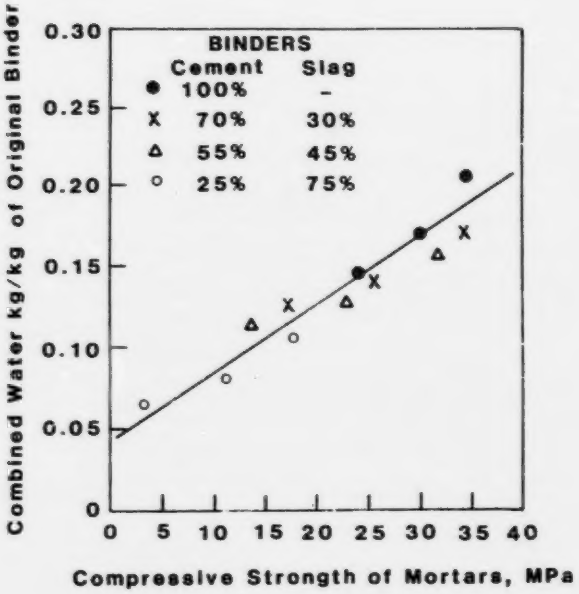

Fig. 6.8 — Relation between combined water and compressive strength (34)

Effect of Activators on Strength Development

Low compressive strength values at early ages obtained in mortars with 65:35 portland cement to copper slag ratio led researchers to the study of the effect of alkaline activators on early strength (4). Atwell (1) reported that when 5 to 10% of precipitator dust with an alkali-oxide content of about 5% was added to mortars made with portland cement–copper slag blends, an increase of up to 25% in compressive strength at seven days was observed.

The effect of calcium carbonate and calcium chloride on air-cooled and on granulated nickel slag was investigated by Laneuville (5) in mortars with 30% portland cement replacement with slag. He concluded that the compressive strength of nickel slag mortars does not improve by increasing its basicity.

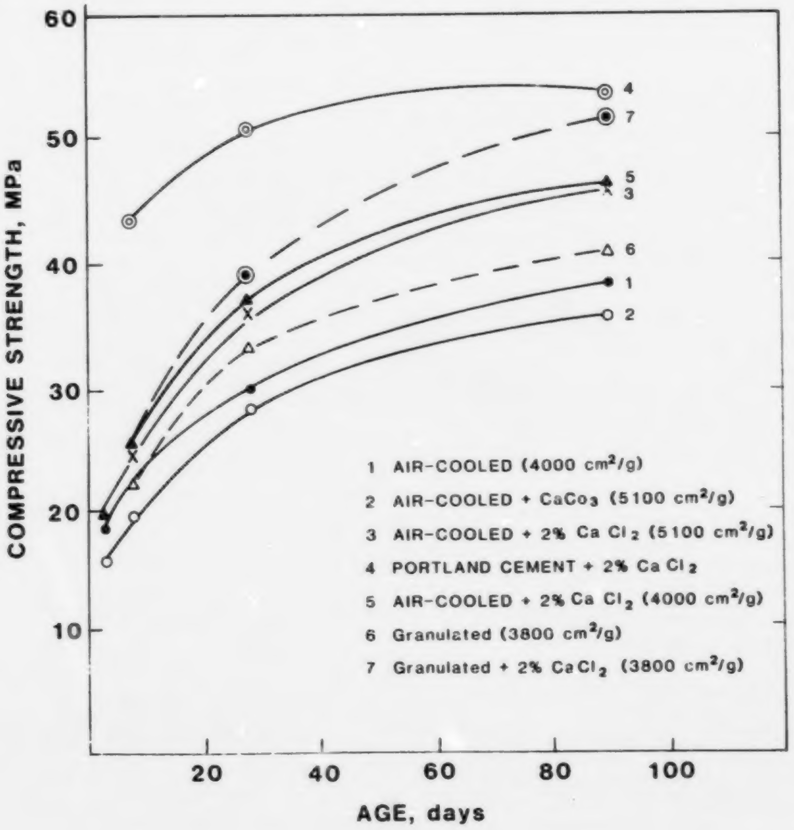

Fig. 6.9 — Effect of activators on compressive strength of air-cooled and granulated nickel slags ground to various finenesses (5)

Activation with calcium chloride was found effective for improving the performance of air-cooled slags after seven days curing (Fig. 6.9). The results showed improvement of strength at all ages in granulated slags with addition of 2% calcium chloride.

Laneuville (5) tested the effectiveness of precipitator dust used as an activator. The kiln dust contained 16.8% potassium oxide and 9.5% free calcium oxide. He concluded that the incorporation of cement precipitator kiln dust in portland cement–nickel slag binders yielded binders with improved early strength characteristics and properties close to those of portland cement mortars.

Recent studies, however, indicate that the activation of lead, nickel, and copper slags by addition of Na(OH) to the mixing water, at a concentration of 200 g/L, or by replacing portland cement by cement kiln dust, does not result in satisfactory performance (10).

7. DURABILITY OF MORTARS INCORPORATING NON-FERROUS SLAGS

The performance of concrete with partial replacement of cement by non-ferrous slags possessing pozzolanic properties is not known. Baragano (4) reported results of tests on mortars on the protective capacity against corrosion for steel reinforcement. Good results were observed for copper slag–cement blends without addition of calcium chloride as an activator.

Baragano (4) has also reported results on tests for resistance to sulphate attack on mortars with copper slag–portland cement blends. Calcium, magnesium, and sodium sulphate solutions as well as sea water were used as aggressive agents. The greatest resistance was shown by a slag cement with 35% copper slag, compared with portland cement mortar or with portland cement blended with 35% natural pozzolan. Similarly, the freezing and thawing tests on mortars indicated better performance with copper slag than with natural pozzolan.

8. CONCLUDING REMARKS

1. Non-ferrous slags appear to have considerable potential for partial portland cement replacement in cemented mine backfill and in concrete.

2. Additional research work needs to be done to define areas of applications as well as limitations on the use of non-ferrous slags.

Suggested Research

A research program directed towards the use of non-ferrous slags in cemented mine backfill and concrete should include:

- development of standards for quality control;
- development of tests for detection of potential health hazard due to leaching of deleterious elements;
- tests for resistance of concrete to external agents.

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